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Adsorption of Organic Cations to Soils and Subsurface Materials

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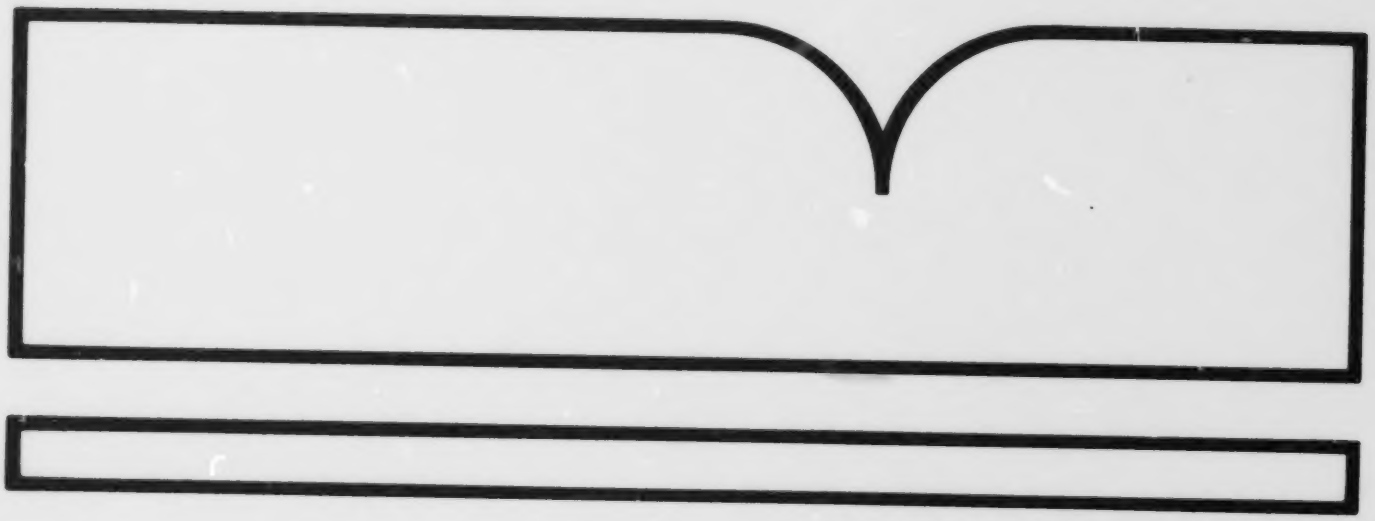

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A study of the fundamentals of adsorption of amphiphilic organic cations on natural and pristine surfaces was conducted to elucidate (i) the factors that influence the extent of adsorption and (ii) indirect effects of adsorption of organic cations: the competitive adsorption of organic cations and metal cations and enhanced adsorption of hydrophobic organic compounds on mineral surfaces coated with organic cations.

The sorbents studied were kaolinite, montmorillonite, silica, alumina, a soil, and two aquifer materials. The distribution ratio of the alkylpyridinium depended strongly on the nature and concentration of inorganic cations in solution, but solution pH had little effect. The adsorption isotherms were distinctly nonlinear. The adsorption of dodecylpyridinium in the presence of various concentrations of salts was described quantitatively with a multisite competitive ion-exchange model. Dodecylpyridinium was found to displace Cu(II) effectively from Lula aquifer material when the surface concentration of dodecylpyridinium is within 10 - 100% of the adsorption maximum. Dodecylpyridinium on Lula aquifer material enhanced the sorption of chlorobenzenes.

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by

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FOREWORD

EPA is charged by Congress to protect the nation's land, air and water systems. Under a mandate of national environmental laws focused on air and water quality, solid waste management and the control of toxic substances, pesticides, noise and radiation, the Agency strives to formulate and implement actions which lead to a compatible balance between human activities and the ability of natural systems to support and nurture life.

The Robert S. Kerr Environmental Research Laboratory is the Agency's center of expertise for investigation of the soil and subsurface environment. Personnel at the laboratory are responsible for management of research programs to: (a) determine the fate, transport and transformation rates of pollutants in the soil, the unsaturated and the saturated zones of the subsurface environment; (b) define the processes to be used in characterizing the soil and subsurface environment as a receptor of pollutants; (c) develop techniques for predicting the effect of pollutants on ground water, soil, and indigenous organisms; and (d) define and demonstrate the applicability and limitations of using natural processes, indigenous to the soil and subsurface environment, for the protection of this resource.

This report presents a study of the adsorption of organic cations to soils and subsurface materials. This information aids in understanding the transport and fate of organic cations in the subsurface environment, and how the presence of these compounds affects the transport and fate of hydrophobic organic compounds and metal ions.

Clinton W. Hall

Clinton W. Hall
Director
Robert S. Kerr Environmental
Research Laboratory

ABSTRACT

A study of the fundamentals of adsorption of amphiphilic organic cations on natural and pristine surfaces was conducted to elucidate (i) the factors that influence the extent of adsorption and (ii) indirect effects of adsorption of organic cations: the competitive adsorption of organic cations and metal cations and increased adsorption of hydrophobic organic compounds on mineral surfaces coated with organic cations.

The sorbents studied were kaolinite, montmorillonite, silica, alumina, a soil, and two aquifer materials. The distribution ratio of the alkylpyridinium depended strongly on the nature and concentration of inorganic cations in solution, but solution pH had little effect. The adsorption isotherms were distinctly nonlinear, even at very low surface concentrations of organic cations. The adsorption of dodecylpyridinium in the presence of various concentrations of salts was described quantitatively with a multisite competitive ion-exchange model; two adsorption reactions were significant: exchange of pyridinium with a metal cation, and adsorption of pyridinium with chloride counter-ion.

The indirect effects of adsorption of organic cations were investigated as well. Dodecylpyridinium was found to displace Cu(II) effectively from Lula aquifer material when the surface concentration of dodecylpyridinium is within 10 - 100% of the adsorption maximum. Dodecylpyridinium on Lula aquifer material increased the sorption of chlorobenzenes; organic-carbon normalized distribution ratios of chlorobenzenes (K_{oc}'s) were greater for DP-loaded sorbents than for natural sorbents, and the values of K_{oc} were greater for greater amounts of dodecylpyridinium on the surface.

The possibility of using amphiphilic organic cations in the subsurface environment to alter the mobility of pollutant metal ions or pollutant hydrophobic organic compounds appears to be worthy of further study. However, further laboratory studies and site-specific information is still necessary for the development of a treatment program.

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SECTION 1

INTRODUCTION

Amphiphilic organic cations are used in a wide range of consumer and industrial products such as detergents, fabric softeners, dyes, herbicides, emulsifying agents, and additives to drilling muds (Greek and Layman, 1989). Adsorption of organic cations influences their bioavailability, transport, and fate. Adsorption can have important indirect effects as well: organic cations can effectively displace adsorbed metal ions, and adsorbed organic cations can increase the affinity of sorbents for hydrophobic compounds. Despite the importance of these compounds, there has not been extensive systematic investigation of their adsorption to soils and subsurface materials.

Direct effects. Organic cations generally adsorb strongly due to the electrostatic attraction to negatively charged surfaces and the favorable hydrophobic interaction. In the environment they are likely to accumulate on surfaces until they are degraded, for example, in sediments downstream from a wastewater discharge, as reported by Lewis and Wee (1983) for ditallowdimethylammonium chloride (DTDMAC).

The environmental concentrations of organic cations have not been surveyed intensively. This situation is largely due to difficulties in separation and analysis of organic cations in natural water samples.

Studies of biotoxicity of organic cations show great variability, but the values of LC_{50} show that the biological impact of these compounds in

the environment must be given careful consideration. For example, Lewis and Suprenant (1983), in a review of the acute toxicities of surfactants to aquatic invertebrates, report 48-hour LC_{50} values of cetyltrimethylammonium in the range of 0.025 - 0.05 mg/L for *D. Magna*. Lewis and Wee (1983) have reported that acute and chronic toxicity levels of DTDMAC and distearyldimethylammonium chloride (DSDMAC) are similarly low for a number of freshwater and marine species, but toxicity was dramatically decreased in natural waters containing increasing amounts of suspended particulates. Addition of slight excesses of an anionic detergent, linear alkylbenzenesulfonate (LAS), was especially effective in increasing the concentration levels of organic cations required to affect test organisms.

One of the primary problems in assessing the environmental safety of organic cations is the characterization of their physical and chemical form (speciation) in test systems. The reductions in toxicity noted above have been attributed to the binding of the compounds to suspended matter in the river water. If meaningful interpretation of laboratory toxicity experiments is to be made, the speciation of the compounds in solution must be known.

Indirect effects. In addition to these direct effects of organic cations in the environment, the indirect effects must be considered. Among these are the influence of organic cations on the mobility of other pollutants, particularly hydrophobic organic compounds and metal ions. Adsorption of organic cations can render mineral surfaces low in organic carbon much more attractive to hydrophobic organic compounds (Cowan and White, 1962; Mortland, 1975; Gaynor and Volk, 1976; Mortland et al., 1986; Bouchard et al., 1988, Lee et al., 1989), and can displace adsorbed metal

ions (Beveridge and Pickering, 1983; Bouchard et al., 1988). Relatively few data on these indirect effects are available in the literature.

While these effects will occur naturally as organic cations are introduced into the environment, they might also be the basis for remedial action at sites already contaminated with metals or hydrophobic organic compounds. The observation that adsorbed organic cations increase the tendency of mineral surfaces to sorb hydrophobic organic compounds has led to consideration of applying organic cations in the subsurface environment (e.g., to clay liners) to slow the migration of organic compounds. However, such a treatment might also lead to desorption and increased mobility of toxic metal ions. On the other hand, if a pump and treat process were being considered, such a displacement of metals with nontoxic, biodegradable organic cations would be beneficial. This study addresses fundamental questions that need to be resolved before these applications are pursued.

Scope of study. The objectives of this study were: (i) to characterize the factors that influence the adsorption of amphiphilic organic cations to natural sorbents; (ii) to describe the observed adsorption isotherms in terms of mechanistically based adsorption models, which can be used for understanding environmental distributions; and (iii) to assess the effect of organic cation adsorption on the adsorption of metals and hydrophobic organic compounds.

The organic cations selected for this study were alkylpyridinium cations; selection criteria include environmental relevance, representativeness of the class, and ease of analysis. The sorbents were aquifer materials, a soil, kaolinite and montmorillonite, and silica and alumina. Efforts were concentrated on well characterized,

low-organic-carbon sorbents. Cu(II) and chlorobenzenes were chosen as representative metal and hydrophobic organic compounds for examination of indirect effects.

SECTION 2

LITERATURE REVIEW

Scope of review.

Two homologous series of cationic surfactants have been commonly employed in adsorption studies: the alkyltrimethylammoniums and N-alkylpyridiniums. The N-alkylpyridiniums were the focus of this study.

The literature was reviewed through citations and a search through Chemical Abstract Service CAS ONLINE (STN International). We searched for articles pertaining to various aspects of the chemistry of decyl-, dodecyl-, tetradecyl-, and hexadecylpyridinium salts. The search covered the years 1967 - 1988; for articles published before 1967, our review relies on citations and is less comprehensive.

Almost all of the adsorption studies involve pure-phase sorbents such as clays, oxides, and textiles. Many of these materials are important constituents or potential analogs of soils and subsurface materials. We have also included a review of references that we have found on adsorption of other organic cations, and on additional aspects of the behavior of cationic surfactants. Whereas a large number of articles were reviewed, only those of direct significance to this study are presented here.

Production and uses of organic cations.

Large amphiphilic organic cations are used in a wide range of commercial and industrial products (Boethling, 1984; Huber, 1984; Greek

and Layman, 1989). The single most important use of cationic surfactants is as fabric softeners. Other important uses are as detergents, germicides, emulsifying agents, and as additives to drilling muds.

Environmental fate and effects of organic cations.

Fate. Cationic surfactants can have direct environmental effects in natural waters, due to their relatively high levels of toxicity to aquatic organisms. Lewis and Suprenant (1983), Lewis and Wee (1983), Boethling (1984), and Huber (1984) review the toxicity and fate of cationic surfactants in surface and waste waters.

Organic cations are likely to accumulate on surfaces until they are degraded, for example, in sediments downstream from a wastewater discharge as reported by Lewis and Wee (1983) for ditallowdimethylammonium chloride (DTDMAC). The environmental concentrations of organic cations have not been surveyed as intensively as the concentrations of many other compounds. This situation is largely due to difficulties in separation and analysis of organic cations in natural water samples.

Degradation. Cationic surfactants are microbially degraded in river and waste waters (Baleux and Caumette, 1977; Games et al., 1982; Boethling, 1984; Huber, 1984; Shimp, 1989). Biodegradation depends on a number of factors, including the presence of oxygen, acclimation period, chemical speciation, and surfactant structure and concentration. Alkylpyridiniums are less susceptible to degradation than are many alkylammonium compounds (Baleux and Caumette, 1977).

Biological effects. Alkylpyridiniums are found to have consistently higher levels of toxicity compared to various alkylammonium surfactants. The presence of anionic surfactants and natural dissolved organic matter

attenuates the toxicity of cationic surfactants, presumably by complexation with negatively charged organic compounds.

Studies of biotoxicity of organic cations show great variability, but the values of LC_{50} show that the impact of these compounds must be given careful consideration. For example, Lewis and Suprenant (1983), in a review of the acute toxicities of surfactants to aquatic invertebrates, report 48-hour LC_{50} values of cetyltrimethylammonium in the range of 0.025 - 0.05 mg/L for D. Magna. Lewis and Wee (1983) have reported that acute and chronic toxicity levels of DTDMAC and distearyldimethyl-ammonium chloride (DSDMAC) are similarly low for a number of freshwater and marine species, but toxicity was dramatically decreased in natural waters containing increasing amounts of suspended particulates. Addition of slight excesses of an anionic detergent, linear alkylbenzenesulfonate (LAS), was especially effective in increasing the concentration levels of organic cations required to affect bioactivity in test organisms. A reduction in toxicity to activated sludge bacteria by octadecyltrimethylammonium on addition of LAS has also been noted (Games et al., 1982).

One of the primary problems in assessing the environmental safety of organic cations is the characterization of their physical and chemical form (speciation) in test systems. Lewis and Wee (1983) attributed the reductions in toxicity of DTDMAC and DSDMAC noted above to the binding of the compounds to suspended matter in the river water. If meaningful interpretation of laboratory toxicity experiments is to be made, the speciation of the compounds in solution must be known (Games et al., 1982; Boethling, 1984). Furthermore, it is likely that interactions among anionic and cationic organic compounds in contaminated ground waters may

lead to significant reductions in toxicity of the compounds, as well as to changes in soil sorption and migration of either species.

Indirect effects

In addition to their toxicological effects, organic cations can have important indirect effects on the environmental behavior of other surface-active pollutant compounds.

Competition with metals. Adsorption of organic cations by clays and soils may effectively displace metals and other adsorbed cations. Beveridge and Pickering (1983) show effective competition of organic cations with Cu, Cd, Pb, Zn, on smectites, moderate competition on illites, and effectively no competition on kaolinite. Bouchard et al. (1988) observed quantitative ion exchange of hexadecylethyldimethyl-ammonium with Ca, Mg, Na, and K on a natural aquifer material, Lula N6.

Enhancement of adsorption of hydrophobic organic compounds. Cationic surfactants adsorbed on low organic carbon soils or clays can enhance the adsorption of other organic compounds by increasing the hydrophobicity of the sorbent material. Gaynor and Volk (1976) found that the presence of cationic surfactants enhanced adsorption of picloram on a number of Oregon soils. The chain length of the organic cation can have large effects on the affinity of organo-clay complexes for phenol (Cowan and White, 1962) and chlorobenzenes (see Mortland, 1975). Bouchard et al. (1988) have shown the binding of nonpolar organic compounds on aquifer material treated with ethylhexyldimethylammonium was greatly enhanced, and that the carbon normalized distribution constants were significantly greater than that observed for octanol or natural organic matter. This observation may be due to the aliphatic character of the organic cation.

Modification of physical properties of soils. Adsorbed organic cation may also affect soil structure, ratability, and colloid stability (Law et al. 1966). Changes in these properties can be expected to have a role in contaminant fate and transport processes in soil and subsurface environments

Adsorption of organic cations on various sorbents.

Adsorption of anionic and cationic surfactants has been reviewed thoroughly by Hough and Rendall (1983). The sorbent materials that have been studied include: oxides, such as silica (Rupprecht et al., 1971; Bijsterbosch, 1974; Harrop, 1978; Huang and Gu, 1987), quartz (Fuerstenau, 1956; Fuerstenau et al., 1964; Somasundaran et al., 1964; Takeda and Usui, 1987; Schwarz et al., 1988), silica-alumina (Vilcu and Oteanu, 1975), and alumina (Fuerstenau and Modi, 1959); AgI sols (Ottewill and Rastogi, 1960); various clay minerals (Greenland and Quirk, 1962; Law and Kunze, 1966; Malik et al., 1972; Ralston and Kitchener, 1975; Qawas et al., 1986); carbon blacks (Saleeb and Kitchener, 1965); polystyrene latex; (Connor and Ottewill, 1971); ion-exchange resins (Tamamushi and Tamaki, 1959); and various textile fibers, which, as organic polyelectrolytes, resemble natural geopolymers in some respects (Sexsmith and White, 1959; Rendall, et al., 1979; Sakata and Katayama, 1987, 1988).

Adsorption isotherms.

Cationic surfactants adsorb strongly onto negatively charged materials due to a combination of hydrophobic and electrostatic interactions. The extent of adsorption depends on properties of the

sorbent, solution, and surfactant. It is often difficult to assess the relative contributions of electrostatic, hydrophobic, and specific chemical interactions, and the degree to which various properties affect those interactions. As a result, the observed adsorption isotherms are nonlinear and often very complex; sigmoidal or S-shaped isotherms are common.

Nonlinearity at low concentrations. At low surface coverage, cationic surfactants adsorb independently of each other. Isotherm nonlinearity in this part of the isotherm can either be due to a decrease in the electrostatic energy as the negative charge of the surface is neutralized by organic cation, or, in the case of heterogeneous natural materials, a filling of higher energy adsorption sites. Unfortunately this part of the isotherm is rarely determined.

Hemimicelle formation at higher concentrations. A steep rise in slope of the concentration of surfactant in the adsorbed phase vs. the solution concentration is then often observed at higher concentrations. The increase has been attributed to lateral sorbate-sorbate interactions of the hydrophobic chains that result in cooperative adsorption effects. The onset of cooperative adsorption on the isotherm has been commonly termed the hemimicelle concentration (HMC) (Fuerstenau, 1956; Fuerstenau et al., 1964). This effect appears to be primarily related to the extent of surface coverage of the surfactant, but may also depend on other properties such as the polarity of the surface, electrolyte concentration and type, and alkyl chain length. When properties that affect the distribution of cationic surfactant on a given surface are varied, such as alkyl homolog number or ionic strength, the HMC occurs over a relatively small range of surface coverages (Connor and Ottewill, 1971; Schwarz et

al., 1988). An HMC is not observed when adsorption is weak and the surface coverage does not reach a critical level (Takeda and Usui, 1987). Typically, the HMC occurs at surface coverages between 0.01 and 0.1 times that of a calculated monolayer (Fuerstenau et al., 1964; Ottewill and Rastogi, 1971; Hough and Rendall, 1983; Takeda and Usui, 1987). The occurrence of a hemimicelle region in the adsorption isotherms of cationic surfactants has been observed for a wide range of materials, but have not been demonstrated well for clays or heterogeneous natural sorbents. This may be due to the difficulty of experimentally accessing the very low concentration range of the adsorption isotherm when the adsorption is very strong.

Steep rises in the adsorption isotherm can be due to phenomena other than hemimicelle formation. An increase in the slope of the isotherm at higher surface coverages can be due to a re-orientation of adsorbed surfactant from a quasi-parallel to a perpendicular orientation. Spectroscopic evidence suggests that cationic surfactants adsorbed to clays reorient to a perpendicular adsorption state at solution concentrations that are below 20 μM (DellaGuardia and Thomas, 1983; Nakamura and Thomas, 1986). Such reorientations are expected to occur at concentrations higher than the HMC, where lateral effects are only beginning to be important. Highly sensitive techniques are required to study sorption of organic cations at pre-HMC concentrations. Multilayer adsorption, which is discussed in the next section, can also cause steep rises in adsorption isotherms.

Adsorption maximum. Ultimately, the adsorption reaches a plateau at higher concentrations. The solution and adsorbed concentrations at which this plateau occurs depend on a number of factors, most important of which

are the affinity of the suriace for cationic surfactants and the hydrophobicity of the organic cation itself. The adsorption energy is affected by properties that influence the electrostatic or hydrophobic interactions. A discussion of electrostatic and hydrophobic interactions, as they influence organic cation adsorption, is found in the discussion of our experimental results that follows.

Maximum adsorption is limited in general at a solution concentration at, or slightly above, the critical micelle concentration (CMC) of the surfactant; the point of maximum surfactant activity. For negatively charged polystyrene latex, active carbon, quartz, and silica the maximum concentration adsorbed corresponds roughly to a calculated monolayer coverage of the surface (Saleeb and Kitchener, 1965; Ottewill and Rastogi, 1960; Bijsterbosch, 1974; Schwarz et al., 1988). At maximum concentration the surface charge is positive, as determined by electrophoretic mobility. Charge reversal due to adsorption of cationic surfactants has been observed to occur on a number of surfaces that are negatively charged at low surfactant concentrations (Fuerstenau,1956; Saleeb and Kitchener, 1965; Connor and Ottewill, 1971; Bijsterbosch, 1974; Rendall et al., 1979). Adsorption can plateau before a monolayer coverage is approached under conditions where adsorption is weaker and becomes limited by surfactant activity near the CMC (Hough and Rendall, 1983). On the other hand, for high energy surfaces, for example clays with large cation exchange capacities (CEC), plateau adsorption can occur at concentrations much below the CMC (Greenland and Quirk, 1962). When plateau adsorption occurs below the CMC, the possibility of multiple layer adsorption is more likely. Multiple layer adsorption has been suggested to interpret adsorption of cationic surfactants onto silica (Ter-Minassian-Saraga,

1966; Bijsterbosch, 1974), montmorillonite (Greenland and Quirk, 1962), and other clays (Malik et al., 1972; Ralston and Kitchener, 1975).

Adsorption of organic cations by natural materials

There have been very few studies on the adsorption of organic cations by natural sorbents. Bouchard et al. (1988) determined adsorption of ethylhexadecyldimethylammonium bromide on the two aquifer materials that have been used in this study, but the focus of that study was not on the organic cation adsorption. Rastogi and Dhawan (1974) measured adsorption of dodecylpyridinium on sandy soils, but only after they had been modified by peroxide and 0.2 M HCl treatments.

In addition to the above mentioned work on cationic surfactants, there have been studies conducted on the adsorption of other large organic cations on clays and natural materials. The adsorption of various herbicides, dyes, tetraalkylammoniums, and mono- and bipyridinium compounds by clay minerals has been well characterized (Weber et al., 1965; 1968; Theng et al., 1967; Weber and Weed, 1968; Weed and Weber, 1969; Philen et al., 1970; 1971; Ghosal and Mukherjee, 1972; Hayes et al., 1978; Narine and Guy, 1981).

The adsorption onto sediments and soil materials of two large organic cations that are not surfactants, paraquat (Karickhoff and Brown, 1978) and methylacridinium (Brown and Combs, 1985) suggest that clay minerals are important constituents of natural materials with respect to adsorption of organic cations and that ion-exchange models may be a valuable approach for describing organic cation distributions. Important conclusions of these studies are: (i) the adsorption was controlled by the clay-sized fraction of the sorbents; (ii) adsorption increased to saturation

concentrations that corresponded closely to the cation exchange capacity of the sorbents; similar results have been seen in studies of adsorption of organic cations on clays (Law and Kunze, 1966; Weed and Weber, 1969; Ghosal and Mukherjee, 1972; Hayes et al., 1978); (iii) adsorption of methylacridinium resulted in a proportional release of metal cations from the soil; the equivalents of metal desorbed averaged 67% of the equivalents of organic cation adsorbed, and the desorbed metal was primarily Ca^{2+} for the most of the ten soils in the study; Greenland and Quirk (1962) found a comparable release of Na^{+} from Na-montmorillonite on adsorption of alkylpyridiniums below the CEC; and (iv) the data for methylacridinium adsorption could be described reasonably well by a competitive Langmuir adsorption equation in which the maximum surface concentration is set equal to the CEC of soil, and all metal ions, other than the organic cation, are lumped together and assigned an empirical K.

Together, these results suggest that clay minerals are important constituents of natural materials with respect to adsorption of organic cations and that ion-exchange models may be a valuable approach for describing organic cation distributions.

SECTION 3

ADSORPTION OF ALKYLPYRIDINIUM TO SOILS AND SUBSURFACE MATERIALS

INTRODUCTION

Large, hydrophobic organic cations find important uses as dyes, herbicides, and surfactants. Cationic surfactants are used in a wide range of consumer and industrial products (Boethling, 1984; Huber, 1984; Greek and Layman, 1989). The single most important use of cationic surfactants is as fabric softeners. Other important uses are as detergents, germicides, emulsifying agents, and as additives to drilling muds. Cationic surfactants adsorb strongly to soils, sediments and suspended particles because of favorable hydrophobic and electrostatic interactions with negatively charged surfaces of natural materials. The toxicity, transport, and fate of organic cations are greatly affected by adsorption to surfaces as well as by association with anionic surfactants or natural dissolved organic matter.

In addition to direct effects, adsorption of cationic surfactants can have important indirect effects on the environmental behavior of other surface-active pollutant compounds; adsorption of cationic surfactants by soils and clays effectively displaces metals from these surfaces (Beveridge and Pickering, 1983; Bouchard et al., 1988); cationic surfactants adsorbed on low organic carbon soils or clays can enhance the adsorption of other organic compounds by increasing the hydrophobicity of the sorbent material (Bouchard et al., 1988; Cowan and White, 1962; Mortland, 1975; Gaynor and Volk, 1976;

Mortland et al., 1986). Despite the importance of these compounds, there has been a lack of systematic investigations on their adsorption to natural materials.

In this part of the study we have examined the adsorption of alkylpyridiniums on natural and other relatively pristine sorbents in order to characterize the properties of the sorbent and the solvent that affect the distribution of large organic cations in the aqueous environment.

METHODS

Materials. ^{14}C-labeled 1-dodecylpyridinium bromide (DP) was synthesized by Pathfinder Laboratories Inc. (St. Louis, Mo.) by refluxing 1-bromo-[1-^{14}C]-dodecane with pyridine. The specific activity was 10.6 Ci/mol and purity of the label was greater than 99% as determined by HPLC with radioactivity detection. Solutions of DP used in this study were checked periodically for purity; no evidence of degradation was found.

Unlabeled DP and 1-hexadecylpyridinium (HP) were purchased as the chloride monohydrates from Aldrich Chemical, and were used as received. The critical micelle concentrations (CMC) of DP and HP in deionized water are 14.7 and 0.99 mM, respectively (Bayer et al., 1986). The critical micelle concentrations of dodecylpyridinium at 25°C in 0.01 and 0.1 M NaCl solutions are estimated from the data of Ford et al. (1966) as 13 and 6.3 mM, respectively.

The sorbent materials used in this study included heterogeneous natural materials (soils and subsurface materials), clays, and silicon and aluminum oxides. The organic carbon contents and cation exchange capacities (CEC) of these materials are given in Table 1. It should be borne in mind that the CEC's are operational parameters, which are not strictly applicable at conditions (solution pH, other solutes, etc.) other than those at which they were determined. The values are given here just for reference and rough comparisons.

The heterogeneous natural materials included low organic carbon ($\leq$ 0.03% organic carbon) aquifer materials Borden sand (Bouchard et al., 1988; Fuller and Davis, 1987) and Lula N6 sorbent (courtesy of Dermont Bouchard, U.S.E.P.A.) (Bouchard et al., 1988), and a relatively high organic carbon (2.3%) EPA-12 soil (Hassett et al., 1980) provided by Professor John J.

Table 1. The cation exchange capacities and organic carbon contents of the natural materials and clay minerals used in this study. Organic carbon contents were determined on a LECO carbon analyzer. Procedures for cation exchange capacity determination are given in the references cited.

Sorbent material	organic carbon %	cation exchange capacity meq/kg
Kaolinite (KGa-1)	0.022	20 (a)
Na-Montmorillonite (SWy-1)	0.020	764 (a)
Borden sand	0.026, 0.020 (b)	7.0 (b), 23 (a)
Lula N6 aquifer material	0.021, 0.033 (a)	90 (a)
EPA-12 soil	2.12, 2.33 (d)	135 (d)

a Bouchard et al., 1988.

b Fuller and Davis, 1987.

c van Olphen and Fripiat, 1979.

d Hassett at al., 1980.

Hassett of the University of Illinois. Georgia kaolin (KGa-1) and Wyoming Na-montmorillonite (SWy-1) (van Olphen and Fripiat, 1979) were obtained from Source Clays Repository at the University of Missouri. Berkeley 5 μm silica and 10 μm MCA-540 alumina were obtained from Pennsylvania Glass Sand Corp. and Alcoa Laboratories, respectively. A 74 - 210 μm fraction of Borden sand, isolated by dry-sieving, was used in this work.

The deionized water used in all experiments was from a Millipore Milli-Q System, with specific resistivity of approximately 18 MΩ cm.

Equipment. For equilibration and phase separation, a thermostatted shaker (New Brunswick Model G-24) and thermostatted centrifuge (Beckman Model J2-21) were used. Concentrations of unlabeled pyridinium compounds were determined spectrophotometrically with a HP 8452A UV-Visible spectrophotometer. Radioactivity of the labeled compounds was determined with a Beckman Model LS 7800 scintillation counter. Labeled compounds adsorbed to aquifer material or soil were converted to $^{14}CO_2$ with a Harvey Model 300 Oxidizer.

Preparation of sorbent materials. The sorbents were pretreated by repetitive washing. The purpose of this step was: (i) to equilibrate the sorbent with the electrolyte solution before addition of pyridinium; and (ii) to reduce the amounts of material that remains suspended in solution after centrifugation. Association of organic compound with nonseparable suspended material (NSM), such as dissolved organic matter or clay sized particles, can affect the observed distributions of organic compounds in batch adsorption experiments (Gschwend and Wu, 1985).

The same general procedure, with minor variations, was used to pretreat the sorbents. A known mass (0.050 - 1.0 g) of sorbent and 20 mL of

electrolyte solution were added to 25 mL Corex glass centrifuge tubes. In general, the electrolyte solutions (various mixtures of NaCl, NaN_3, and $CaCl_2$) were those to be used in the distribution experiments that followed the pretreatment. In the case of EPA-12 soil, the particles were washed with deionized water instead of electrolyte solution to facilitate comparison of results to previous work on adsorption of anionic and neutral surfactants with the same sorbent (Zhang et al., in prep; Brownawell et al., in prep.). For clay materials, a predetermined volume of HCl or NaOH was added to maintain an initial pH of 6.5.

The tubes were shaken for periods of 30 minutes to 6 hours at 500 RPM and 25°C in a thermostatted shaker. Then the suspensions were centrifuged for 5 - 30 minutes at 5,300 - 9,100 RPM (4,000 - 11,000 G) and 25°C. The longer equilibration and centrifugation times were used for clays. The supernatant was removed and replaced with fresh electrolyte solution. The entire procedure was repeated a total of 5 - 8 washes before the sorbents were used in distribution experiments.

Determination of distributions. Distributions were determined from batch equilibration experiments. Two different procedures were used for introducing the alkylpyridinium compounds to the electrolyte solution and the pretreated sorbents: (i) the unlabeled compounds were dissolved in the electrolyte and added directly to the sorbent, and (ii) for the labeled compounds, the following procedure was used. First the pyridinium-free electrolyte solution was mixed with the sorbent and the suspension was centrifuged. Then the particle-free solution was spiked with DP in 10 - 200 μL of 95% ethanol. The purpose of this procedure was to reduce the

likelihood of contact between sorbents and localized high concentrations of DP during the spiking.

The electrolytes were NaCl, NaN_3, and $CaCl_2$. NaN_3 was used in place of NaCl in experiments conducted at low concentration of DP to minimize potential microbial degradation (Zhang et al., in prep.). The contents of the tubes, which were sealed with PTFE-lined caps, were mixed on the shaker at a speed of 500 RPM at 25°C for 4 hours, after which the aqueous and sorbent phases were separated by centrifugation at 11,000 G at 25°C for 30 - 60 minutes.

After centrifugation, we determined the amount of alkylpyridinium in the aqueous phase, adsorbed to the sorbent, and adsorbed to the walls of the vessel. The analytical procedures are described below. The concentration distribution ratio and recovery (% of alkylpyridinium added to the tube that could be accounted for by analysis) were calculated from these data. The concentration distribution ratio, D_c, was calculated from:

$$D_c = \frac{C_i(s) \quad (\mu mol/kg)}{C_i(w) \quad (\mu M)} \qquad (1)$$

where $C_i(s)$ and $C_i(w)$ are the concentrations of the component i determined directly in the sorbed and water phases, respectively.

Analysis for labeled pyridinium. Aliquots of the aqueous phase were obtained for ^{14}C-labeled dodecylpyridinium analysis with a graduated glass pipette and transferred to scintillation vials containing 10 mL of Beckman RP scintillation fluid. The concentration of DP adsorbed to sorbent material was determined by oxidizing two subsamples (10 - 200 mg) from each tube at 900°C in the oxidizer. The $^{14}CO_2$ was trapped directly in a

scintillation vial in a mixture of 5 mL Packard Carbo-sorb and 5 mL Permafluor V scintillation fluid. The walls of the centrifuge tubes were then brushed clean, 20 mL of 95% ethanol were added to extract DP adsorbed to the walls, the tubes shaken for 20 minutes, and 1 mL aliquots were sampled as described for the aqueous phase. The activity of ^{14}C-labeled compound in each sample was determined by counting at least 10,000 counts, and converting to decay rate through a H# correction (Horrocks, 1977). Calibrations were performed for each experiment by adding various amounts of DP to each phase, and determining activity. The calibrations were linear and the counting efficiency was regularly 93 and 75% for the aqueous and solid phase samples, respectively. The overall precision for aqueous and sorbent samples was generally less than 2 and 5% RSD, respectively. These procedures produced very good recoveries of DP; the average recovery for all experiments was 97% and the average relative standard deviation within an individual experiment was 1.5%.

Analysis of unlabeled pyridinium. Separate analysis of sorbent- and wall-adsorbed pyridinium was not performed routinely when experiments were conducted with higher concentrations of unlabeled compounds; at higher concentration, adsorption of DP onto centrifuge tube walls was negligible, and the amount of HP adsorbed to the walls from 100 μM solutions represented 1 - 7% of the amount in solution. Aqueous phase samples were collected with a 5 mL Oxford pipet for UV and pH analysis. The concentration of alkylpyridinium was determined by UV spectrophotometry in a 1 cm cell at 260 nM (ϵ = 4100 AU M^{-1} cm^{-1} for alkylpyridinium). After the remaining aqueous phase was removed from the centrifuge tube, the pellet was resuspended and adsorbed pyridinium was extracted with 20 mL of methanol or

0.01 M HCl in methanol. The tubes were shaken for 1 hour and centrifuged; the extract was analyzed for concentration of alkylpyridinium by UV spectrophotometry as above. These procedures resulting in complete recovery of alkylpyridinium adsorbed to Borden sand, Lula aquifer material, and kaolinite clay; recoveries were not complete for silica, alumina, and montmorillonite. In the case of the latter sorbents, the amount adsorbed was estimated from the difference between final and initial aqueous phase concentrations.

pH experiments. The influence of $[H^+]$ on the distribution of alkylpyridinium was examined with several sorbent materials. Various volumes of 1.0 M NaOH and HCl were added to sorbent suspensions containing organic cation in 20 mL of 0.01 M NaCl or NaN_3. An Orion Model 8102 Ross combination glass electrode, with 4 M KCl outer filling solution was used for pH determination. The electrode was calibrated with buffers certified at pH 4.00, 7.00, and 10.00 from Micro Essential Laboratory (Brooklyn, NY).

Sorption kinetic experiments. Experiments were run to determine the time required for DP to approach equilibrium during adsorption and desorption. For adsorption kinetics, tubes containing 0.05 - 1.0 g of sorbent in 20 mL of solution were prepared and spiked with alkylpyridinium as described above. The tubes were left on the shaker for various times, ranging from 0.5 to 30 hours. For desorption kinetics, sorbents were first equilibrated with pyridinium under identical conditions for 4 hours. Then the solution and sorbent were separated by centrifugation, and the supernatant was discarded and replaced with the same pyridinium-free

electrolyte. The tubes were then shaken concurrently and sampled at various times ranging from 0.5 to 8 hours.

There was relatively rapid adsorption equilibrium for DP in experiments conducted with Borden sand, Lula aquifer material, and montmorillonite. The D_c approaches an apparent equilibrium value within 4 hours of shaking for the two natural materials, after which D_c remains constant over 24 - 30 hours; adsorption was complete for montmorillonite within the first 30 minutes.

The release of dodecylpyridinium from the experiment with Lula sorbent was rapid and nearly reversible; the D_c determined after a 1-hour desorption step was 7330 compared to a D_c of 5800 after the adsorption step.

RESULTS

The objectives of this study were: (i) to characterize the factors that influence the adsorption of large organic cations to natural sorbents; and (ii) to describe the observed adsorption isotherms in terms of mechanistically based adsorption models, that can be used for understanding environmental distributions. The achievement of these objectives is complicated by two fundamental limitations. First, the nonlinearity of the isotherms precludes a simple interpretation of the effects of given properties on the energy of adsorption. We have ascribed much of the nonlinearity to the heterogeneity of adsorption sites of natural sorbents, and have used a distribution of adsorption site energies in describing experimental results. Second, it is difficult, if not impossible, when studying aqueous suspensions of solid adsorbents to vary one experimental parameter and maintain all others at constant values (Zhang et al., in prep.). For example, in the present work, the concentration of H^+ in solution increased due to adsorption of organic cation, and a change in solution pH can affect surface charge and extent of adsorption of organic cation.

We present first the results from experiments in which the adsorption of dodecyl- and hexadecylpyridinium were determined as a function of sorbent and solution composition. A quantitative interpretation and model follow in the discussion section.

Adsorption isotherms. The logarithmic adsorption isotherms of dodecylpyridinium on five different materials are shown in Figure 1. The sorbents (Borden sand, Lula N6 aquifer material, EPA-12 soil, kaolin, and montmorillonite) were pretreated as described earlier; their properties are

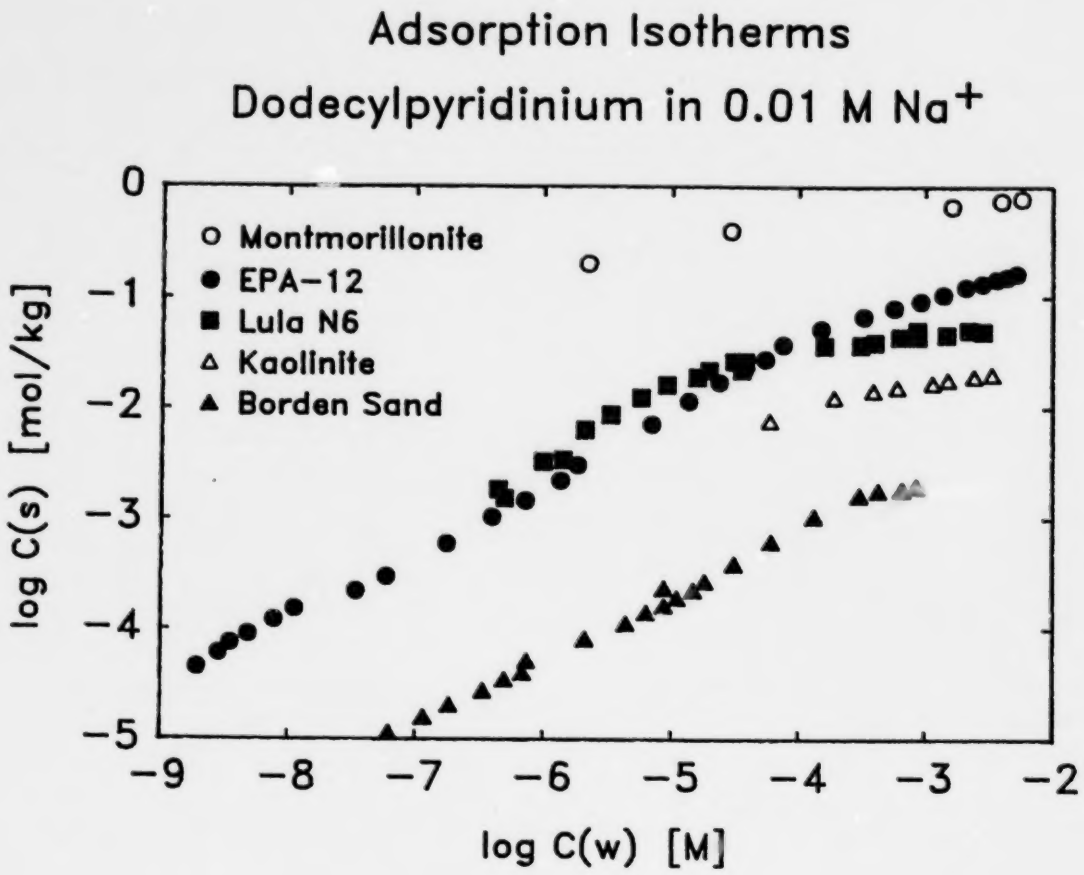

Figure 1. Logarithmic adsorption isotherms of dodecylpyridinium on different materials: montmorillonite (○), ratio of solids to liquids ($C_s(w)$) was 0.0050 kg/L; kaolinite (△), $C_s(w)$ = 0.025; sediment EPA-12 (●), $C_s(w)$ = 0.025; Lula aquifer material (■), $C_s(w)$ = 0.0025; and Borden sand (▲), $C_s(w)$ = 0.025 or 0.050 kg/L. Solutions contained 0.01 M Na^+.

given in Table 1. The aqueous phase contained either 0.01 M NaCl or 0.01 M NaN_3; independent tests indicated no dependence of adsorption on the anion. The equilibrium concentrations of dodecylpyridinium in solution were well below the critical micelle concentration (CMC) in all cases. .

The affinities of the sorbents for dodecylpyridinium, per unit mass of sorbent, follows the order montmorillonite > EPA-12 soil ≈ Lula aquifer material > kaolinite > Borden sand. This order corresponds roughly to the CEC's of the materials. A judgment about the presence or absence of a correlation with organic carbon content of the materials is not warranted, since the organic carbon content of most of these materials is so very low. However, the adsorption affinity of Lula aquifer material is similar to that of EPA-12 despite the 100-fold difference in organic carbon contents of these sorbents.

At concentrations of DP in solution below 125 μM for EPA-12 and Borden sand, and below 20 μM for Lula aquifer material, the logarithmic isotherms (Figure 1) are nearly linear and conform to the logarithmic form of the Freundlich equation:

$$\log C_s = n \log C_w + \log K \qquad (2)$$

where K and n are constants. The values of n determined from the slopes of the isotherms in the low concentration region are 0.63 and 0.58 for EPA-12 and Borden sand, respectively. These low values of n (n = 1 for a linear isotherm) indicates nonlinearity in the isotherms at very low surface coverages. The nonlinearity extends to surface concentrations that are as low as 0.018 % of the maximum surface coverage measured in the case of EPA-12 soil. As will be discussed, this nonlinearity is attributed to heterogeneity of adsorption sites.

The lack of an upward inflection in the slopes of the isotherms over a broad concentration range is significant. A steep rise in slope of the concentration of cationic surfactant in the adsorbed phase vs. the solution concentration is observed on many surfaces at surface concentrations that are between 1 and 10% of a calculated monolayer coverage (Takeda and Usui, 1987; Connor and Ottewill, 1971; Hough and Rendall, 1983; Fuerstenau et al., 1964). The concentration at which the increase in slope occurs is termed the hemimicelle concentration (HMC) (Fuerstenau, 1956; Fuerstenau et al., 1964). Hemimicelles form when the attractive interaction among adsorbed molecules becomes significant compared to the interaction between adsorbed molecules and the surface. The absence of a hemimicelle-formation region in the isotherm is consistent with (i) the heterogeneity of the surface and (ii) the strong interaction between the adsorbed organic cations and the negatively charged surface.

The higher-concentration data from these isotherms are presented in the linear form in Figure 2. The surface concentration reaches or approaches a plateau level, with the exception of EPA-12 isotherm in which the concentration adsorbed is still increasing at 7.9 mM concentration. The plateau concentrations of DP adsorbed correspond closely, but not strictly, to the reported cation exchange capacities measured for the five sorbent materials, as can be seen by comparing Figure 2 to the CEC values given in Table 1. The adsorption affinity of the three natural sorbents at low DP concentration (at 1 μM, for instance) shows a similar trend to the adsorption capacity, except that at low DP concentrations Lula aquifer material has a 1.5 - 2 times greater affinity for DP than does EPA-12.

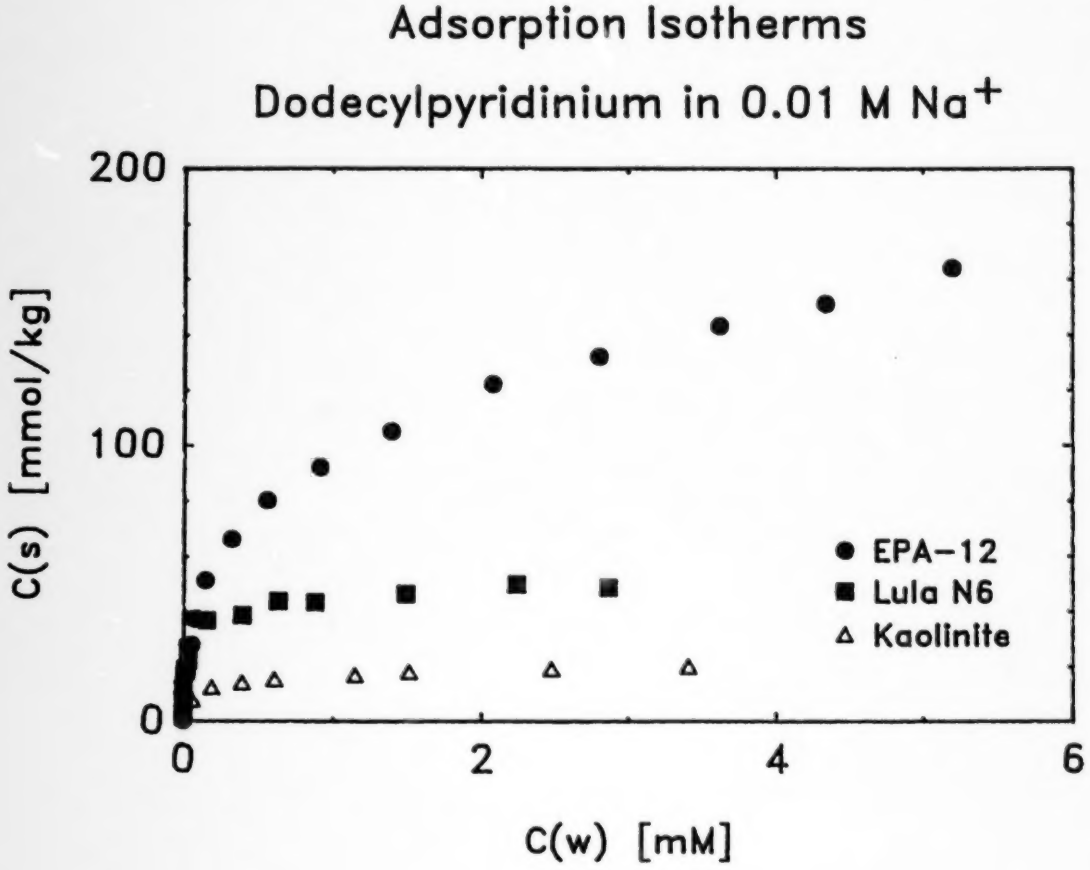

Figure 2. Adsorption isotherms of dodecylpyridinium on different materials; data are from the high concentration range of Figure 1, plotted here on a linear scale. Note the correspondence between the plateaus of the adsorption isotherms and the cation exchange capacities listed in Table 1. Solution contained 0.01 M Na^+; ratio of solids to liquids are given in Figure 1.

Figure 2A. kaolinite (Δ), pH = 5.39 - 4.72; sediment EPA-12 (●), pH = 7.43 - 7.00; and Lula aquifer material (■), pH = 6.81 - 4.49;

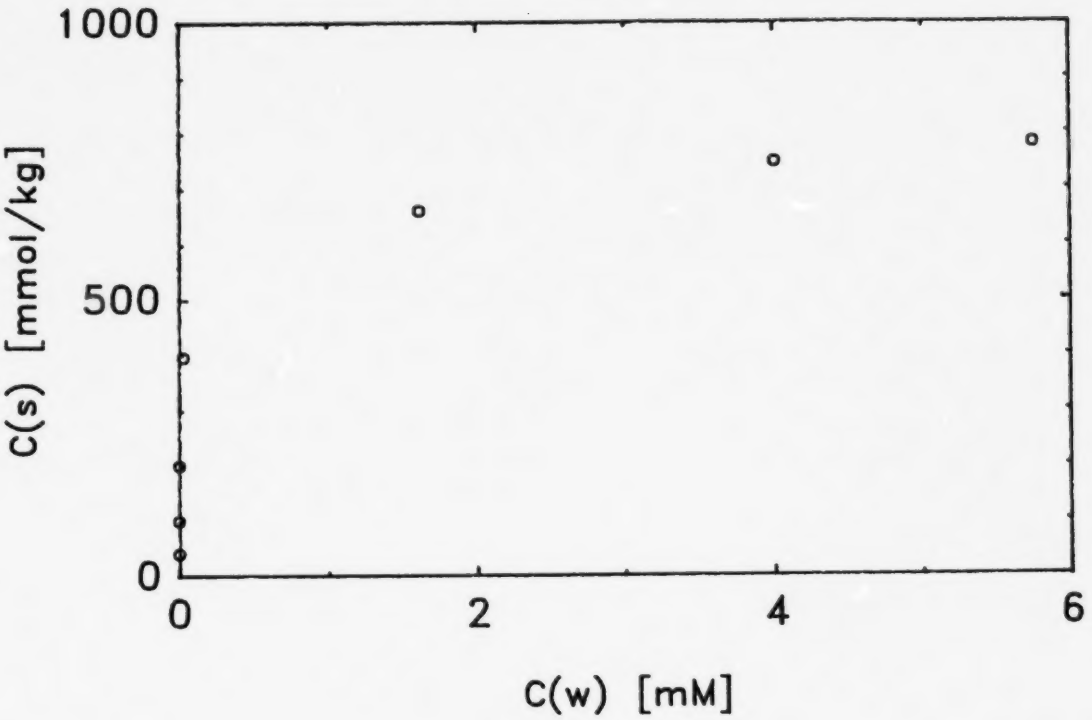

Figure 2B. montmorillonite (●), pH = 7.13 - 5.46;

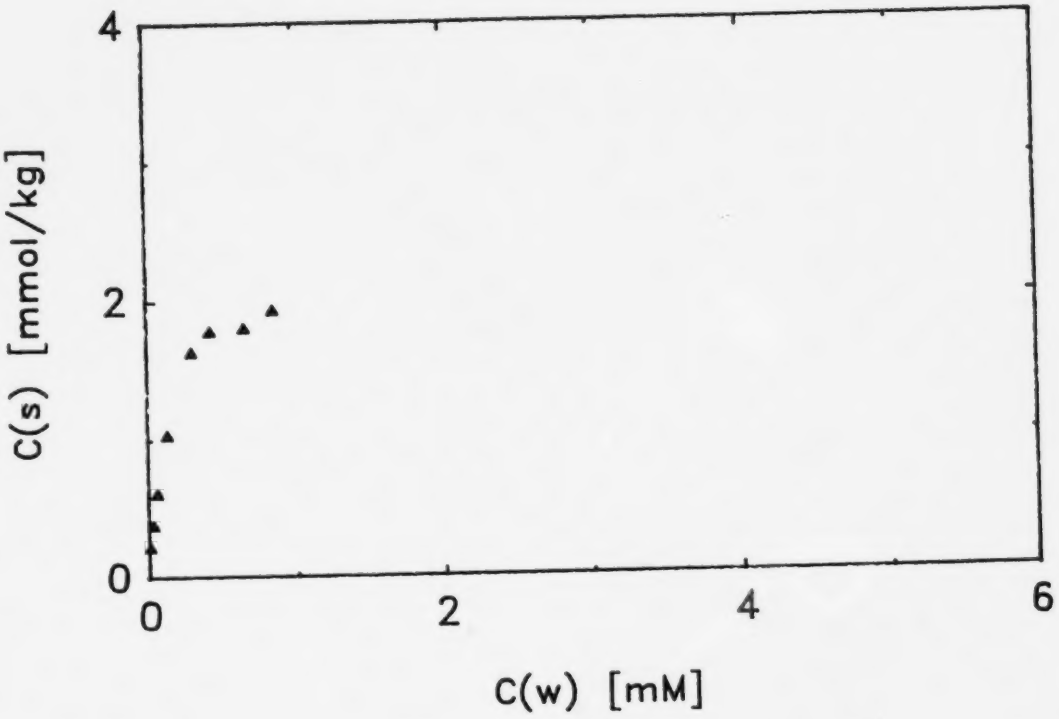

Figure 2C. Borden sand (▲), pH = 9.39 - 9.02.

The effect of pH on adsorption of DP. The relation of solution $[H^+]$ to pyridinium adsorption can be viewed from two perspectives: (i) influence of pyridinium adsorption on $[H^+]$, and (ii) influence of $[H^+]$ on pyridinium adsorption.

A decrease in pH occurred as a result of adsorption of DP on kaolinite, montmorillonite, and Lula aquifer material; the extents of the pH changes are given in the captions of Figure 2. A similar result was observed for adsorption of 1-alkylpyridinium bromides on Na-montmorillonite (Greenland and Quirk, 1962). There is an exchange of H^+ from the sorbent on adsorption of organic cation, despite the fact that the sorbents have been pre-equilibrated with Na solutions. The decrease in solution pH can affect the adsorption of DP by a small amount.

The effect of $[H^+]$ on the adsorption of DP by EPA-12, Lula aquifer material, and kaolin is shown in Figure 3a. The logarithm of D_c is plotted against log $[H^+]$. A very small dependence of D_c on pH was observed for the natural sorbents; the slopes ($\Delta \log D_c / \Delta \log [H^+]$) determined from linear regression of the data in Figure 3a were -0.04 and -0.01 for Lula and EPA-12, respectively. Adsorption of pyridinium increases as $[H^+]$ decreases due to either (i) a change in surface potential resulting from deprotonation of ionizable functional surface groups, or (ii) ion-exchange of H^+ for pyridinium. The very slight effect of pH on adsorption to natural materials provides confidence with regard to the interpretation of the adsorption isotherms in which pH changed due to adsorption of DP. The dependence of log D_c on pH for kaolinite was greater than for the natural materials. At pH values ≤ 6.06 the slope $\Delta \log D_c / \Delta \log [H^+]$ was -0.23.

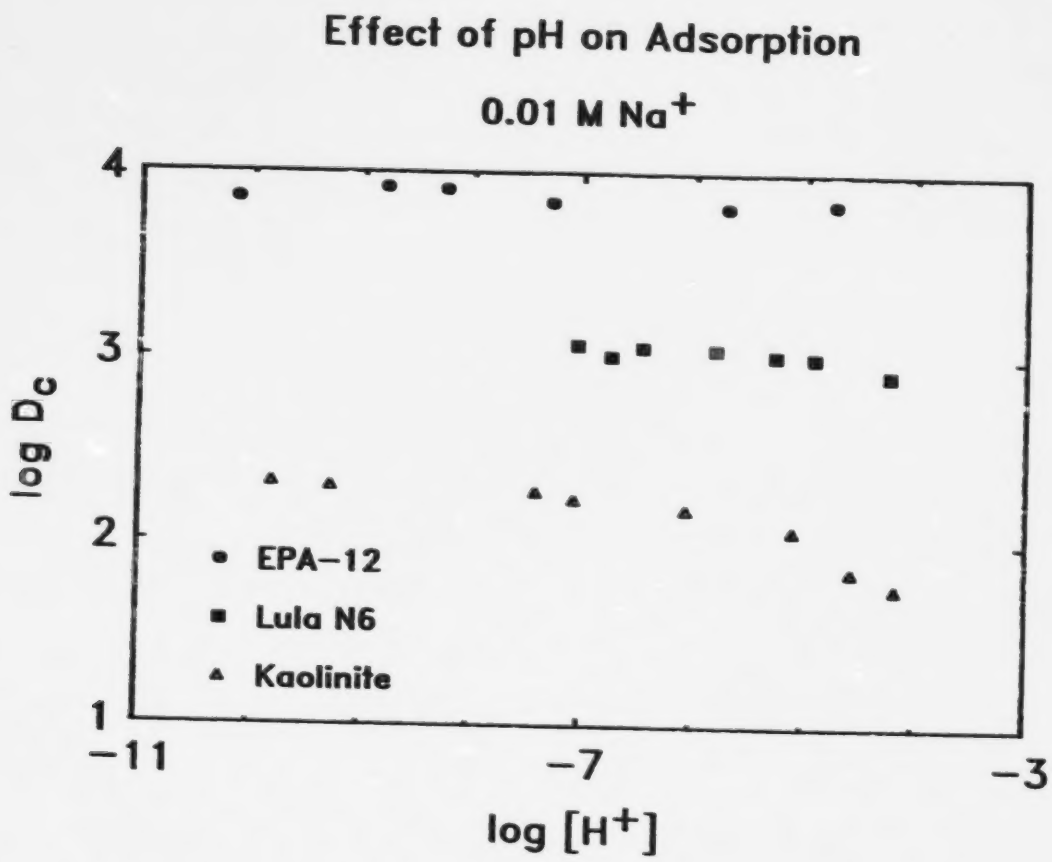

Figure 3. Effect of log [H^+] on the concentration distribution ratio D_c of alkylpyridiniums between aqueous solutions and selected sorbents. Solution contained 0.01 M Na^+. The amounts of dodecylpyridinium adsorbed to the surface were nearly constant for EPA-12 and Lula sorbents: $C_R(s)$ = 0.20 and 29 μmol/g, respectively. $C_R(s)$ ranged from 7.6 - 15 μmol/g for kaolinite.

Figure 3A. dodecylpyridinium on EPA-12 (●), $C_s(w)$ = 0.015 kg/L; Lula (■), $C_s(w)$ = 0.0025; and kaolinite (▲), $C_s(w)$ = 0.0125;

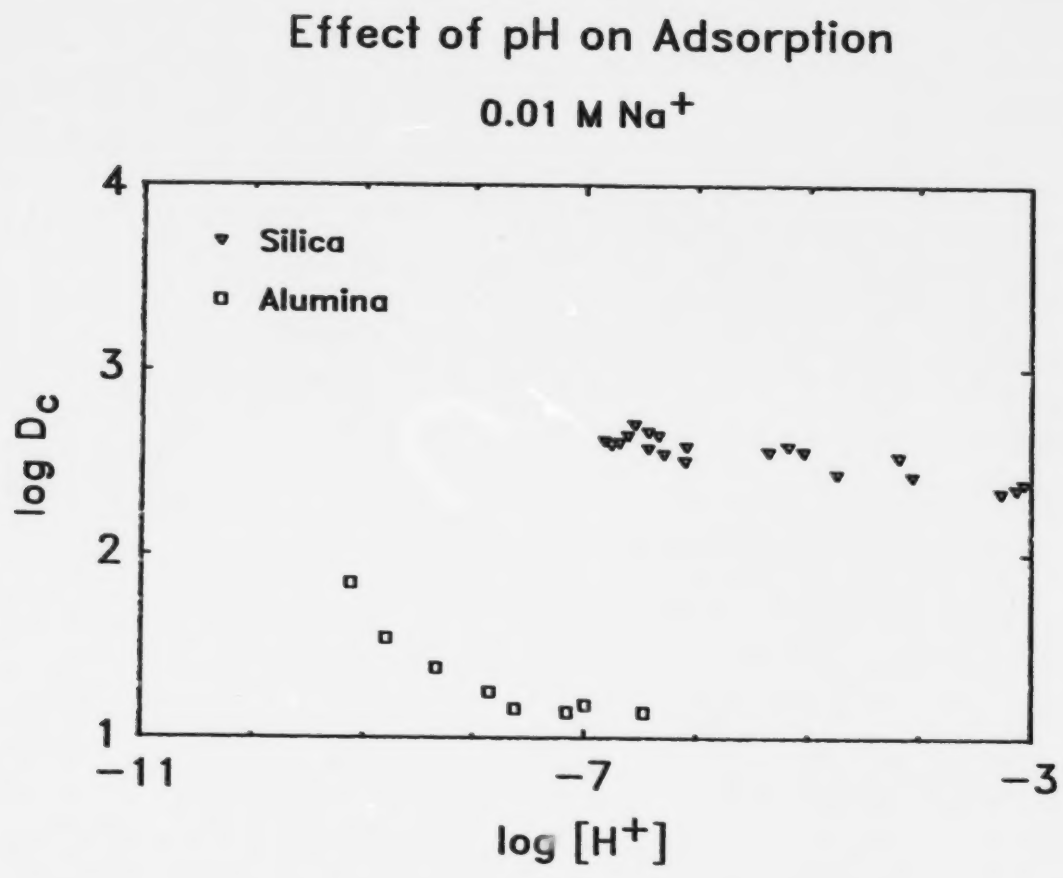

Figure 3B. hexadecylpyridinium on silica (▽), $C_s(w) = 0.0125$; and alumina (□), $C_s(w) = 0.025$.

The effect of $[H^+]$ on HP adsorption by silica and alumina is illustrated in Figure 3b. Experiments were conducted with hexadecylpyridinium for these adsorbents because of the low adsorption of DP on these oxides. The initial concentrations of HP in all experiments were 100 μM. Therefore the differences in D_c between the two materials are due to the properties of the sorbents themselves. Adsorption is favored on the silica, because of its negative charge over this pH region (Iler, 1979).

For alumina, D_c increases slightly with pH up to about pH 7.9, at which point D_c increases dramatically with pH. Two factors may contribute to the dramatic increase in adsorption at higher pH: (i) the reversal of pH-dependent surface charge in the range pH 8 - 9 (Davis and Gloor, 1981); and (ii) cooperative adsorption, as in hemimicelle formation. The surface concentrations in this experiment (1.0 - 2.6 μmol/g) exceeded the surface concentration (1.0 μmol/g) at which hemimicelles appeared to be formed in another experiment (not shown) conducted under similar conditions.

For silica, the value of $\Delta \log D_c / \Delta \log [H^+]$ was - 0.07. The scatter in the distribution data presented in Figure 3b was due in part from incomplete removal of colloidal silica under our separation procedure, which interfered with the observed UV absorption signal. The concentration of the colloidal silica was small and should not have influenced the observed distribution, however.

<u>The effect of electrolyte on adsorption</u>. The effect of concentration and type of electrolyte on adsorption of DP was examined with two complementary types of data: (i) adsorption isotherms of DP from solutions with different concentrations of salts; and (ii) concentration distribution ratio of DP as a function of concentration of NaCl or $CaCl_2$, with a

constant amount of DP in the system. In view of the nonlinearity of the isotherms, the first method is preferable for development of mechanistic models, while the second provides a quick estimate of the magnitude of the effect.

The effect of the salt concentration was generally much greater than that of pH. Figures 4a and 4b show the isotherms of DP on Lula aquifer material in the presence of 0.01 and 0.1 M NaCl, and 0.001 M $CaCl_2$.

At low concentrations of organic cation, an increase in the salt concentration decreases the adsorption by a nearly constant factor. This behavior is consistent with an ion-exchange mechanism. At high concentrations of the organic cation, the isotherms merge and cross at surface concentrations that correspond roughly to the CEC. This behavior is consistent with the predominance of adsorption of pyridinium-chloride at high concentrations of DP. Similar isotherms (not shown) were obtained for Borden sand and kaolinite.

The effect of Ca^{2+} on the adsorption of DP on Lula aquifer material is shown in Figure 4b. It is seen that 0.001 M Ca^{2+} impedes adsorption of DP more effectively than 0.01 M Na^{+}; this result is expected if DP adsorbs predominantly by ion exchange.

The effect of $[Na^{+}]$ on the adsorption isotherm of DP on EPA-12 soil is shown in Figure 5a. It is similar to that described for Lula aquifer material (Figure 4a), except not as pronounced. An explanation for the difference is presented with the quantitative model in the discussion section.

The isotherm of DP on EPA-12 in the presence of $CaCl_2$ and 0.01 M NaN_3 is shown in Figure 5b. (The adsorption in the absence of Ca^{2+} is given by the solid line.) Addition of 0.0006 M $CaCl_2$ had no significant

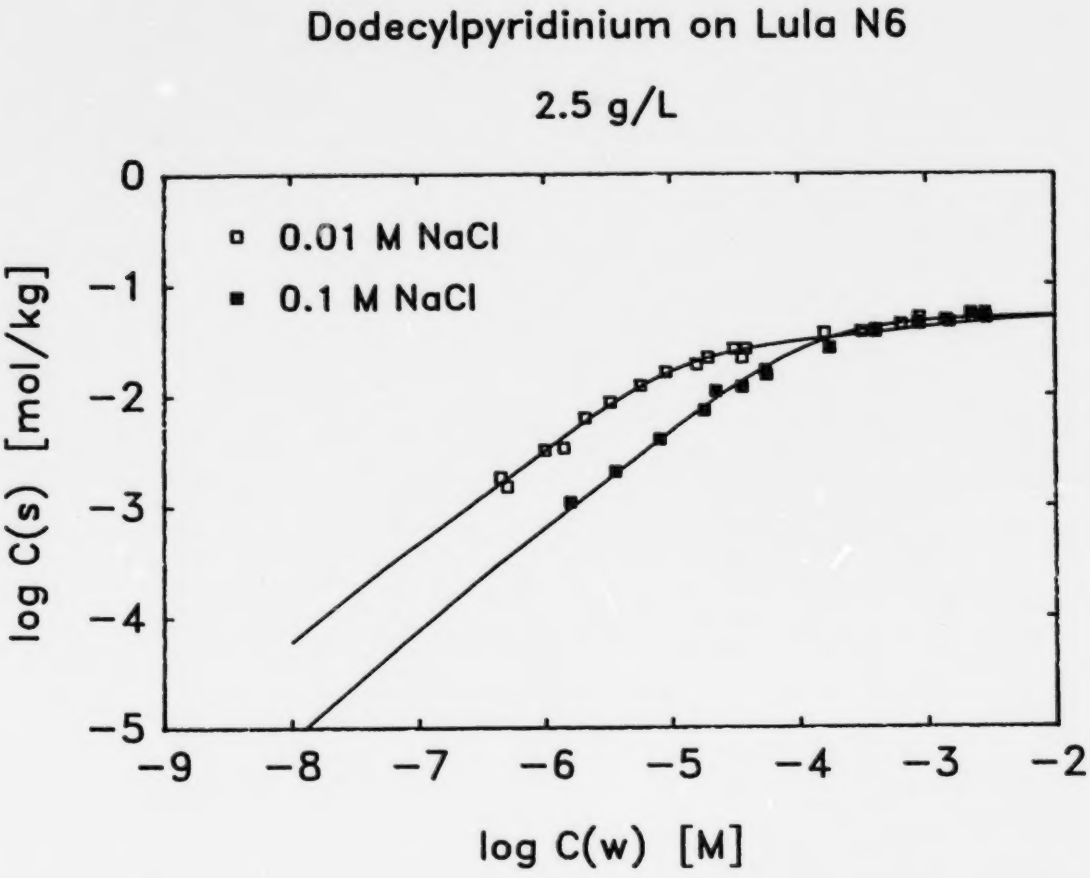

Figure 4. Logarithmic adsorption isotherms of dodecylpyridinium on Lula aquifer material from different salt solutions. The ratio of solids to liquid was 0.0025 kg/L. The solid lines in Figure 4A were computed from the model defined in Table 2; the lines are reproduced in Figure 4B to allow comparison of the effects of Na^+ and Ca^{2+}.

Figure 4A. 0.1 M Na^+ (■) and 0.01 M Na^+ (□);

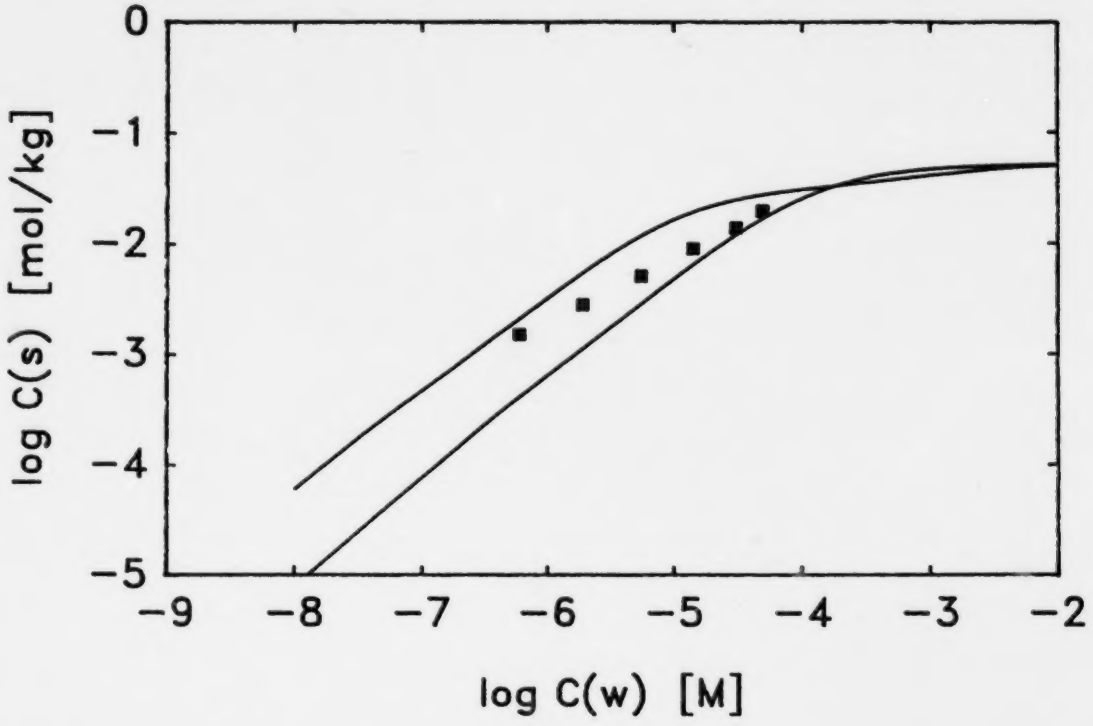

Figure 4B. 0.001 M Ca^{2+} (■). The lines are reproduced from Figure 4A.

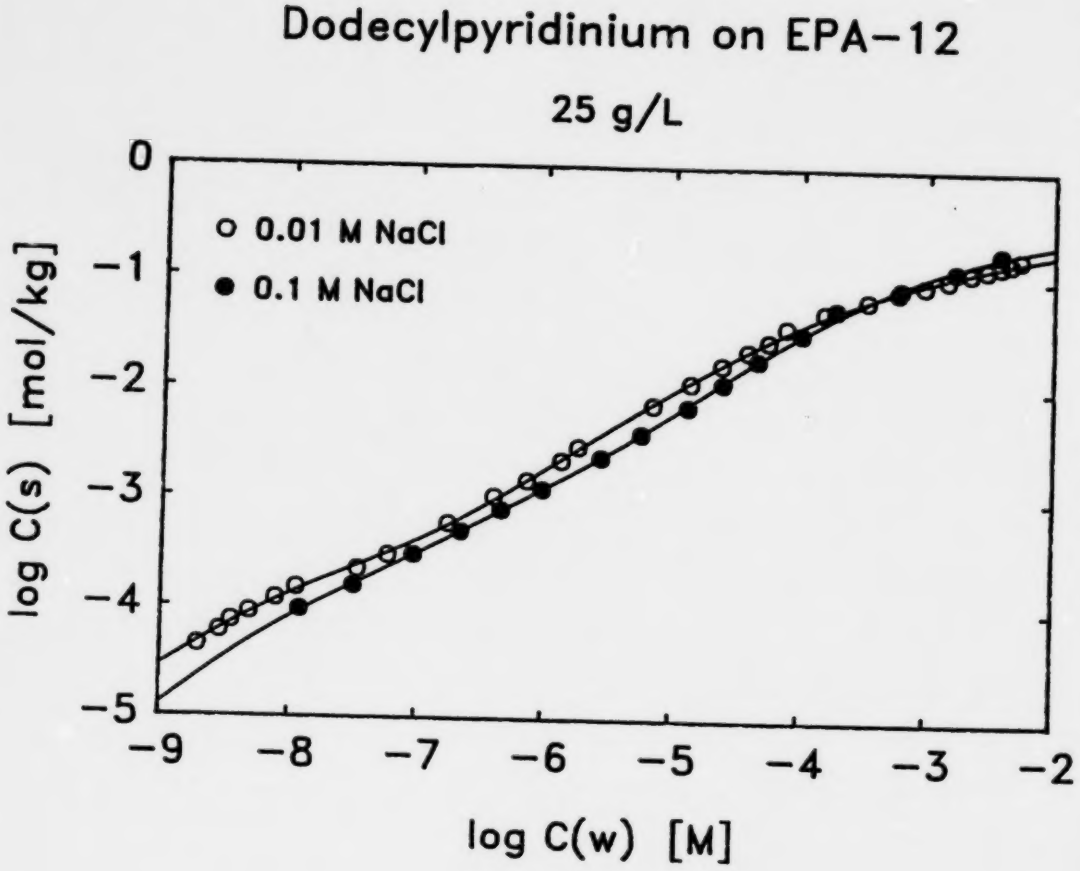

Figure 5. Logarithmic adsorption isotherms of dodecylpyridinium on sediment EPA-12, from different salt solutions. The ratio of solids to liquid was 0.0025 kg/L in A and 0.0050 kg/L in B. The solid lines in Figure 5A were computed from the model defined in Table 3. The line for 0.01 M Na^+ is reproduced in Figure 5B to allow comparison of isotherms in the absence and presence of added Ca^{2+}.

Figure 5A. 0.01 M Na^+ (o); 0.1 M Na^+ (●);

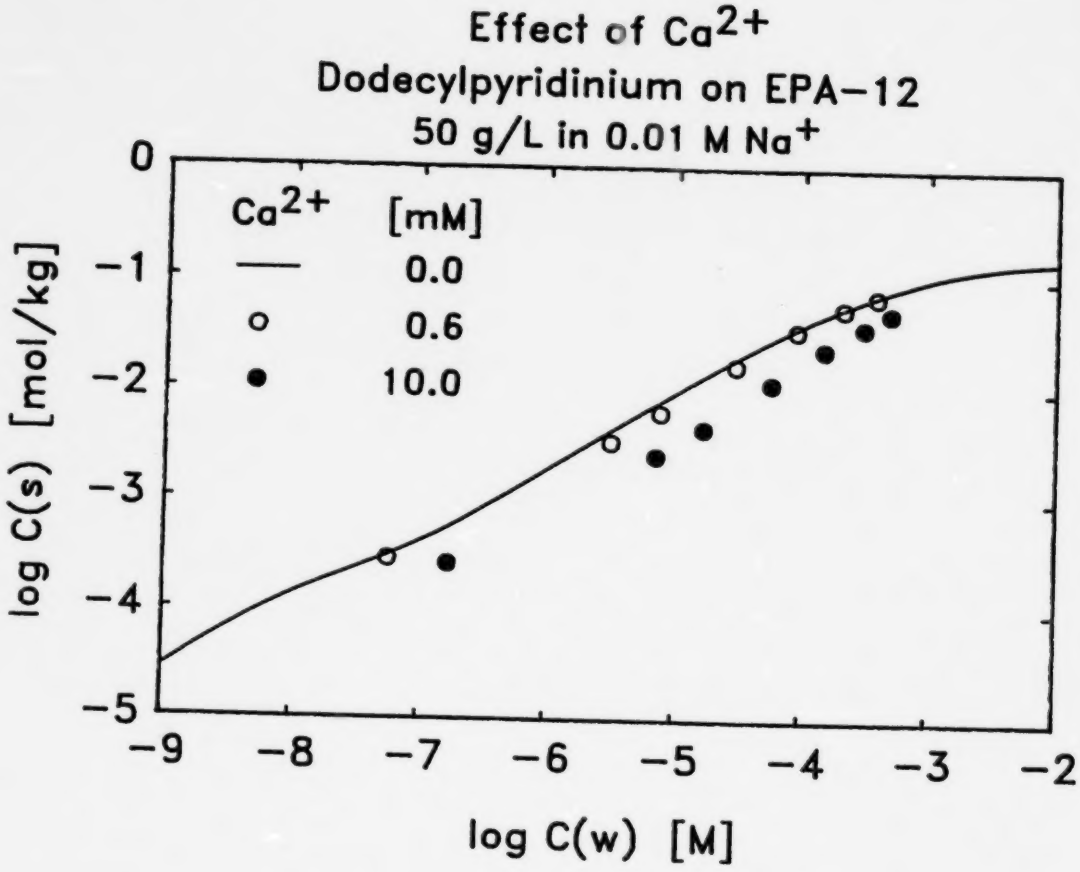

Figure 5B. 0.01 M Na^+ plus 0.0006 M Ca^{2+} (○) and 0.01 M Na^+ plus 0.01 M Ca^{2+} (●). The line was reproduced from Figure 5A for 0.01 M Na^+.

effect on adsorption. Addition of 0.01 M $CaCl_2$ decreased adsorption by a nearly constant factor ($\Delta \log D_c \approx 0.4 - 0.45$, at constant $C_R(w)$). The isotherms with and without added Ca^{2+} tend to merge at the highest concentrations.

Experiments in which the amount of DP was kept constant and the concentrations of supporting electrolyte were varied, showed effects on adsorption that were similar to those observed in isotherm studies. The effects of added $CaCl_2$ in the presence of 0.01 M NaN_3 on D_c for both EPA-12 and Lula are illustrated in Figure 6. The effects are similar for both sorbents. At low $[Ca^{2+}]$, the change in D_c with change in $[Ca^{2+}]$ is small due to the masking effect of the 0.01 M Na^+ background electrolyte. At $[Ca^{2+}]$ above 1 mM, the dependence of log D_c on log $[Ca^{2+}]$ is approximately linear; the slope of $\Delta \log D_c / \Delta \log [Ca^{2+}]$ is -0.49 and -0.44 for EPA-12 and Lula, respectively.

The influence of added NaCl on the adsorption of DP by EPA-12 soil is given in Figure 7. The D_c for DP with EPA-12 soil decreases 0.50 log units as the $[Na^+]$ is increased from 0.01 to 0.1 M. The value of $\Delta \log D_c / \Delta \log [Na^+]$, excluding the lowest Na^+ concentration datum, is -0.62, similar to that observed for Ca^{2+}.

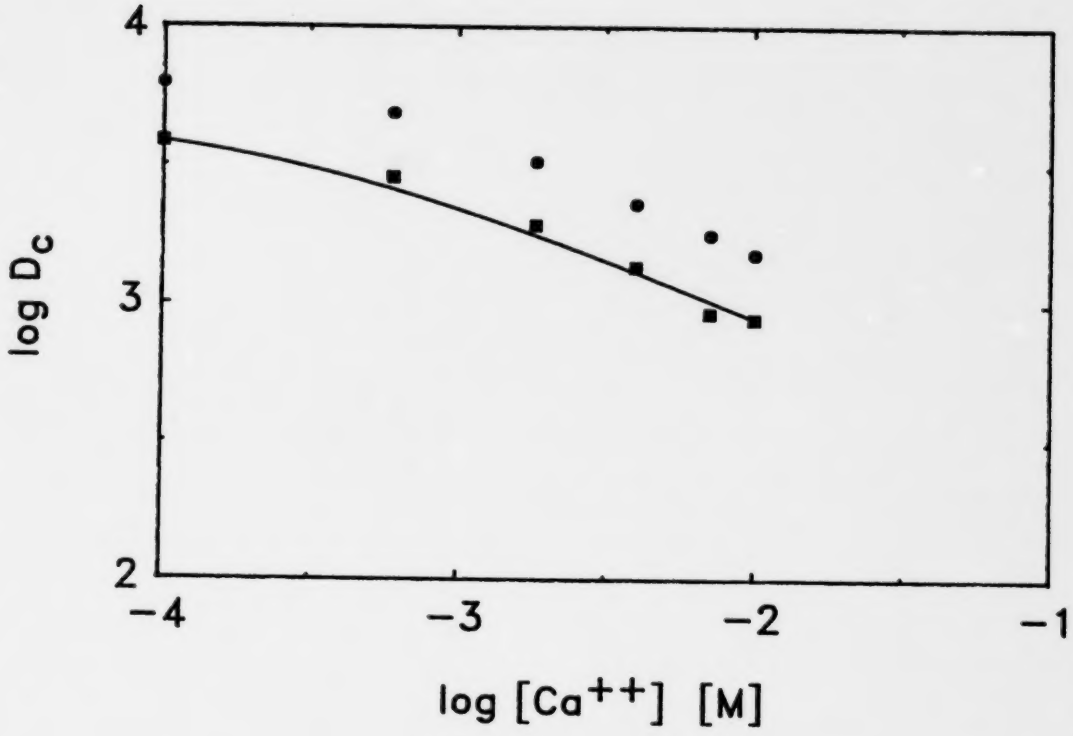

Figure 6. Effect of [Ca^{2+}] on the concentration distribution ratio D_c of dodecylpyridinium on sediment EPA-12 (●) and Lula aquifer material (■), in 0.01 M Na^+. The solid line was computed from the model defined in Table 2. The amounts of dodecylpyridinium on the surface in these experiments were approximately constant at 415 μmol kg^{-1} (Lula) and 275 μmol kg^{-1} (EPA-12); the amount of solids was 0.0025 kg L^{-1} (Lula) and 0.005 kg L^- (EPA-12).

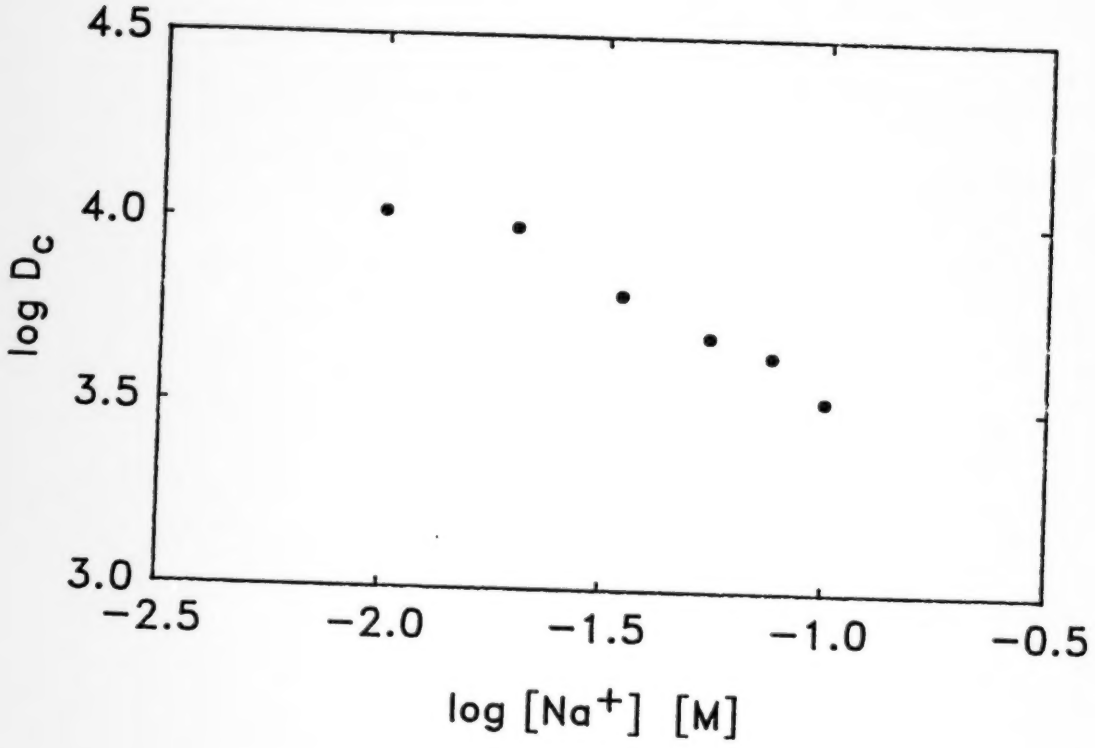

Figure 7. Effect of [Na^{2+}] on the concentration distribution ratio D_c of dodecylpyridinium on sediment EPA-12 (•). The amounts of dodecylpyridinium on the surface were approximately constant at 290 μmol kg^{-1}, and the amount of solids was 0.0050 kg L^{-1}.

DISCUSSION

In this study we have determined isotherms for the adsorption of an organic cation on natural sorbents and have examined some of the properties of solution and sorbent that affect the distribution. The following questions are important in the interpretation of these results: (i) how can nonlinear isotherms be interpreted quantitatively and mechanistically? (ii) what type of adsorption model can account for the strong dependence of adsorption on electrolyte and relatively weak dependence on pH? (iii) why are cooperative effects absent from the adsorption isotherms determined with natural material? and (iv) what properties of sorbent, solvent, and solute are most important in determining the extent of adsorption of large organic cations on natural materials?

Nonlinear isotherms. All of the adsorption isotherms determined in this study were nonlinear, even at very low surface coverages of dodecylpyridinium (Figure 1). (A linear isotherm is one in which the surface concentration is directly proportional to the solution concentration, i.e., $n = 1$ in Equation 2.) Causes of isotherm nonlinearity include: (i) non-uniformity of energies of adsorption sites, with saturation of high-affinity sites; (ii) sorbate-sorbate interactions such as repulsive electrostatic interactions or cooperative chain-chain interactions, and (iii) experimental artifacts that stem from covariation of experimental conditions, such as changes of pH, major ion concentrations, or aggregation of particles, that accompany changes in organic cation concentrations.

For reasons to be discussed, we interpret the nonlinearity of isotherms in these experiments primarily as the result of heterogeneity of sites. Particularly in the low-concentration regions of the isotherms, the changes

in pH, concentrations of major ions in solution, and surface charge that accompanied adsorption of the organic cation were too small to account for the isotherm nonlinearity. Thus, at low concentrations of organic cation, heterogeneity of sites is the preferred explanation. At higher concentrations it is more difficult to exclude the influence of other processes on isotherm nonlinearity.

The nonlinear isotherms are described adequately by the Freundlich equation (Travis and Etnier, 1981) (Equation 2) up to surface coverages of 20% of the CEC, and, with the possible exception of EPA-12 soil, approach a plateau or saturating level as the concentration is further increased. However, the Freundlich equation provides no clear basis for determining intrinsic adsorption energies or adsorption mechanisms (Adamson, 1976).

The mechanistic models that were considered for these data were (i) multisite models, (ii) electrostatic models, and (iii) some combination of the two. Most of the phenomena observed in this study can be explained readily through the multisite model, with electroneutral reactions and no explicit electrostatic energy term. While this approach is obviously an approximation, it is consistent with a variety of observations, and it is conceptually very simple. The role of electrostatic energy will be examined in a future study involving adsorption and electrophoretic mobility.

Adsorption model. The adsorption model that we use is based on the following reactions:

$$R^+ + \overline{NaX} = \overline{RX} + Na^+ \qquad K_{RX} \qquad (3)$$

$$R^+ + Cl^- + \overline{Y} = \overline{RClY} \qquad K_Y \qquad (4)$$

$$Ca^{2+} + 2\,\overline{NaX} = \overline{CaX_2} + 2\,Na^+ \qquad K_{CaX2} \qquad (5)$$

where the overbar represents a species associated with the sorbent, X is a negatively charged cation-exchange site, Y is an uncharged site (that could be thought of as a site for hydrophobic adsorption), and R^+ represents the alkylpyridinium. The mass action equations for Reactions 3-5 are:

$$(R^+)\ \{\overline{NaX}\}\ K_{RX} = \{\overline{RX}\}\ (Na^+) \qquad (6)$$

$$(R^+)\ (Cl^-)\ \{\overline{Y}\}\ K_Y = \{\overline{RClY}\} \qquad (7)$$

$$(Ca^{2+})\ \{\overline{NaX}\}^2\ K_{CaX2} = \{\overline{CaX_2}\}\ (Na^+)^2 \qquad (8)$$

where (i) represents the activity of species i in solution (mol L^{-1}) and {i} represents concentrations of species i on the sorbent (mol kg^{-1}).

The ion exchange sites X and the adsorption sites Y are subject to the following material balance conditions:

$$T_X = \{X\} + \{NaX\} + \{RX\} + 2\,\{CaX_2\} \qquad (9)$$

$$T_Y = \{Y\} + \{RClY\} \qquad (10)$$

where T is the total number of sites (mol kg^{-1}).

Finally, in order to represent the heterogeneous surface, we use not just a single type of site as indicated by X above, but an ensemble of types of sites (X_1, X_2, ... X_n), each of which obeys its own mass action equations and material balance equations given above. A similar approach could be used for the Y sites. Thus the model could be described as a multisite competitive Langmuir model.

The adjustable parameters in the model are the equilibrium constants given by Equations 6-8 and the total number of sites, given in Equations 9 and 10. For the X-sites, the discrete equilibrium-constant-spectrum approach was used: the values of K_{HXi} were set to integral powers of ten (10^0, 10^1, ...) and the total concentration of each type of sites was determined, T_{Xi}. The objective of this approach is to represent the experimental data in terms of a regular distribution of sites, rather than the smallest number of adjustable parameters. This approach facilitates comparison of complex isotherms obtained for different sorbents.

All parameters were determined simultaneously with FITEQL 2.0 (Westall, 1982a, 1982b), a weighted nonlinear least squares adjustment procedure for multicomponent chemical equilibrium problems.

Application of model. This model was applied first to the adsorption of DP on Lula aquifer material. In the first step, data at two different concentrations of Na^+ (Figure 4a) were used to determine the T_{Xi} of the equilibrium-constant spectrum; since only one type of sites Y were considered, both K_Y and T_Y were determined. The constants are given in Table 2, and the isotherms calculated from the constants are given by the lines in Figure 4a. The agreement between the model and the data is excellent. In a second step, the competition by Ca^{2+} was taken into the

Table 2. Equilibrium constants for adsorption of dodecylpyridinium on Lula aquifer material.

Type of Site	Equilibrium Constants[a,b]			Total Site Density
	$\log K_{RX}$	$\log K_{CaX2}$	$\log K_{YRCl}$	mol kg^{-1}
X_1	5.00	3.00		2.89×10^{-4}
X_2	3.00	0.57		3.21×10^{-2}
Y			4.95	1.99×10^{-2}

[a] Reactions described in text, Reactions 3, 4, 5. Equilibrium constants valid for 25 ± 2 °C, with aqueous concentrations in mol L^{-1} and concentrations on sorbent in mol kg^{-1}. Properties of sorbents listed in Table 1.

[b] Constants were determined by the following procedure: values of K_{RX} were set according to the equilibrium constant spectrum approach, and values of T_X, T_Y, and K_{YRCl} were determined from data in Figure 4a with FITEQL (Westall, 1982a; 1982b). Then values of K_{CaX2} were determined from the Lula data in Figure 6 with FITEQL.

model. The equilibrium constants for exchange of Ca^{2+} with each of the NaX_i groups were determined from the Lula data in Figure 6. Again the agreement between the model, shown by the line in Figure 6, and the data is excellent.

The same method of data treatment was used for the adsorption of DP on EPA-12, as shown in Figure 5a. Because the data for adsorption on EPA-12 span six orders of magnitude, the spectrum approach was used for the Y sites as well as for the X sites. The equilibrium constant spectra are given in Table 3 and the amount adsorbed calculated from the model is given by the lines in Figure 5a. The agreement between the lines and the data is very good.

Certainly this "discrete equilibrium-constant-spectrum" approach is subject to the criticism that a model can be fit to any set of data if enough adjustable parameters are used. Furthermore, there is some covariance among the values of the adjustable parameters; the values are not unique, but just one of an infinite number of sets that can be used to represent the data.

However, the advantages of this approach are significant, too. The practical advantage is that the effects of multiple interactions in complex systems can be represented in a way that is completely compatible with chemical equilibrium models used in environmental chemistry. An adsorption isotherm that conforms closely to the Freundlich equation over more than six orders of magnitude range in C(w) can be described very well by conventional mass action and material balance equations; these equations have a mechanistic basis, which potentially could be used to understand the factors that influence adsorption.

Another advantage of such a model is that it provides a framework for evaluating quantitatively mechanisms that could be responsible for the

Table 3. Equilibrium constants for adsorption of dodecylpyridinium soil EPA-12.

Type of Site	Equilibrium Constants[a,b]		Total Site Density
	$\log K_{RX}$	$\log K_Y$	mol kg^{-1}
X_1	7.00		2.07×10^{-5}
X_2	6.00		1.71×10^{-4}
X_3	4.00		8.12×10^{-4}
X_4	3.00		5.87×10^{-3}
X_5	2.00		4.77×10^{-2}
X_6	1.00		5.36×10^{-2}
Y_1		9.00	8.13×10^{-5}
Y_2		7.00	8.37×10^{-4}
Y_3		5.00	2.59×10^{-2}
Y_4		4.00	9.06×10^{-2}
Y_5		3.00	6.50×10^{-2}

[a] Reactions described in text, Reactions 3 and 4. Equilibrium constants valid for 25 ± 2 °C, with aqueous concentrations in mol L^{-1} and concentrations on sorbent in mol kg^{-1}. Properties of sorbents listed in Table 1.

[b] Constants were determined by the following procedure: values of K_{RX} and K_Y were set according to the equilibrium constant spectrum approach, and values of T_X and T_Y were determined from data in Figure 5a with FITEQL (Westall, 1982a; 1982b).

phenomena that are observed experimentally, such as, (i) reversal of effect of electrolyte concentration on isotherms near the CEC; (ii) lateral shift of isotherms with salt concentration far below the CEC; (iii) absence of pH effect; (iv) relative effect of Na vs. Ca on the isotherms; and (v) absence of evidence for hemimicelle formation. The interpretation of these phenomena in terms of the model will be discussed next.

Reversal of effect of electrolyte concentration. An increase in adsorption of DP with increase in concentration of electrolyte is observed to occur at surface concentrations near the CEC (Figures 4a and 5a), or when the normally negative charge of the surface is neutralized. This increase is due to adsorption of RClY, after the exchange sites NaX are fully converted to RX. Higher concentrations of counter-ions enable more DP to accumulate at the surface. The crossover of adsorption isotherms at approximately the CEC observed in this work is consistent with the increase in adsorption of DP with increasing ionic strength on vinylon and acetate (Sakata and Katayama, 1987; 1988), and counter-ion adsorption above the "equivalence point" determined for silica (Bijsterbosch, 1974), celluosic fibers (Sexsmith and White, 1959) and montmorillonite (Greenland and Quirk, 1962).

Lateral shift of isotherms with electrolyte concentration. At concentrations far below the CEC, the isotherms of pyridinium on EPA-12 and Lula are seen to shift laterally with changes in electrolyte concentration (Figures 4a and 5a). If adsorption were due exclusively to the exchange reaction (Reaction 3) and surface activity coefficients were constant, the isotherms should shift a decade with a decade change in salt concentration. In reality the shift is about 0.7 units / decade $[Na^+]$ for Lula and

0.3 - 0.5 units / decade [Na^+] for EPA-12. This attenuation in the shift is explained through adsorption of RClY (Reaction 4), which increases with Cl^- concentration, in contrast to RX, which decreases with Na^+ concentration. Since the formation of RClY is probably related to the hydrophobic effect, it is consistent that the formation of this species is favored on the sorbent with the higher organic carbon content.

pH effect. Adsorption to the heterogeneous natural materials is seen to be virtually independent of pH. Therefore pH-dependent sites, such as organic carboxylic acid groups or surface hydroxyl groups, are not included in the model for these materials.

Effect on isotherms of Ca(II) vs. Na(I). The reduction in adsorption of DP in Ca^{2+}-solutions relative to Na^+-solutions (Figure 4b) is explained in part by the fact that Ca^{2+} competes more effectively for ion-exchange sites of soils and clays. The selectivity coefficient for alkylammonium ions is orders of magnitude greater for Na-montmorillonite than for Ca-montmorillonite (Theng et al., 1967). Diquat adsorption is much reduced on Ca^{2+}-saturated three-layer clays compared to the same clays in the Na^+-saturated form (Weed and Weber, 1968). The effects of Ca vs Na are consistent with cation-exchange of organic cations with the negatively charged sites associated with clay minerals that are present in natural sorbents, but are not consistent with a simple attenuation of long range electrostatic energy due to an ionic strength effect.

Absence of hemimicelles. The formation of hemimicelles at surfaces can be observed when the attractive interaction among adsorbed molecules becomes significant compared to the interaction between adsorbed molecules and the surface. The absence of a hemimicelle-formation region in the isotherm is consistent with (i) the heterogeneity of the surface and (ii) the strong interaction between the adsorbed organic cations and the negatively charged surface.

Hydrophobic interactions. In this study we present little data for compounds other than C-12 pyridinium; thus it is difficult to say much about the effect of hydrophobicity of the sorbate. However, the magnitude of this effect can be estimated from the effect of alkyl chain length on air-water adsorption and micelle formation. An increase in the chain length corresponds to a ΔG° of approximately 2500 J/mol per $-CH_2-$ group, or a $\Delta \log K \approx 0.44$ (Tanford, 1980). The dependence of adsorption on the chain length of anionic LAS surfactants on sediments is $\Delta \log D_c / \Delta n_{-CH2-}$ of 0.40 to 0.45 (Zhang et al., in prep.; Hand and Williams, 1987). These values are close to those observed for adsorption of cationic surfactants on surfaces of quartz (Fuerstenau et al., 1964) and organic polyelectrolytes (Connor and Ottewill, 1971; Rendall et al., 1979). The effect of different headgroups on adsorption can be related to the effective chain length (Ottewill and Rastogi, 1960). The influence of alkyl chain length diminishes as surface saturation is approached. However, cationic surfactants of longer chain length may be packed more closely in a monolayer (Connor and Ottewill, 1971), and are more likely to adsorb in multiple layers (Greenland and Quirk, 1962).

The effect of surface properties on the hydrophobic interaction is more difficult to estimate. It is established that the sorption of nonpolar organic compounds with soils and sediments is controlled by the organic matter fraction of the sediment (Karickhoff et al., 1979; Schwarzenbach and Westall, 1981). However, no correspondence of organic matter content with adsorption intensity was observed for the sorbents examined in this study. Dodecylpyridinium adsorbed more strongly onto Lula aquifer material than onto EPA-12 soil, even though the organic carbon content of EPA-12 was 100 times greater than that of Lula. The one phenomenon that did correlate with organic carbon content of these two materials was the shift in isotherm with electrolyte concentration, as discussed above.

Electrostatic interactions: the effects of pH and supporting electrolyte concentration. Although there is no explicit electrostatic term in the adsorption model, the importance of electrostatic energy is recognized and the topic warrants discussion.

The importance of the electrostatic attraction of DP with negatively charged surfaces of natural particles is perhaps best supported by comparing the distribution ratios with EPA-12 soil in this study to distributions of anionic and neutral surfactants of similar size determined with the same material (Zhang et al., in prep; Brownawell et al., in prep.). The D_c of DP with EPA-12 soil in 0.01 M NaN_3 is estimated as 2010 mL/g at a C_w for DP of 1.0 μM from the Freundlich equation. The estimate of D_c under the same conditions for dodecylbenzenesulfonate is 68.6, and for three nonionic tridecylethoxylates, containing three to nine ethoxyl groups, is 229 to 401.

Electrostatic interactions arise when there is a preferential accumulation of charge at the surface. The surface charge can originate from several processes: (i) preferential dissolution of ions from a mineral surface; (ii) pH-dependent ionization of surface functional groups, such as carboxylic acid groups of organic matter or hydroxyl groups of oxides; (iii) isomorphic substitutions of ions in crystal matrices, as occurs with clays such as montmorillonite (ion-exchange resins with permanently charged functional groups could logically be included in this category); and (iv) preferential adsorption of ions from solution. In formulating electrostatic models to describe adsorption phenomena it is important to recognize that adsorption of an ion from bulk solution requires adsorption of a counter-ion or desorption of a co-ion. The arrangement of surface charge and counter charge, and the type of mathematical model necessary to describe the distribution of ions, depend on the nature of the interface.

Electrostatic models have not been applied commonly to adsorption of ionic organic compounds by soils or sediments. Westall (1986, 1987) has discussed the practical aspects of several electrostatic models that are commonly applied in environmental chemistry. Zhang et al. (in prep.) describe the application and limitations of a double layer model in a study of linear alkylbenzenesulfonate adsorption on sediments. The use of electrostatic double layer models to understand the adsorption of large organic cations has been limited (Takeda and Usui, 1987; Rendall et al., 1979; Hough and Rendall, 1983). A Donnan distribution model has been recently used to describe the dependence of supporting electrolyte concentration on the adsorption of dodecylpyridinium by vinylon and acetate fibers (Sakata and Katayama, 1987; 1988). A Donnan model is strictly more appropriate when the surface is "rough" and electroneutrality is maintained

in the Donnan phase as counter-ions are inside the plane of surface charge; in classical double layer models, electrostatic energies are calculated for counter-ions arranged in layers parallel to the plane of the primary surface charge.

Hydrogen ion activity affects adsorption of organic cations on several surfaces that possess ionizable functional groups (Takeda and Usui, 1987; Bijsterbosch, 1974; Connor and Ottewill, 1971; Rendall et al., 1979). The absence of an appreciable effect of pH on the adsorption to natural materials (Figure 3a) indicates that a pH-dependent surface charge has a minor influence on the electrostatic interaction. The influence of $[H^+]$ on adsorption may be greater when the concentrations of counter-ions that balance the surface charge are lower than the 0.01 M NaCl used in this work.

The effect of increasing concentration of electrolyte is to reduce the adsorption of organic cations on negatively charged surfaces by attenuating the electrostatic energy or through competitive adsorption of co-ion; adsorption on positively charged surfaces is facilitated by attenuation of repulsive electrostatic interactions, or by counter-ion adsorption. This crossover effect was observed in this study (Figure 4a and 5a) and in studies where the intrinsic surface charge is reversed by adsorption of organic cations (Rendall et al., 1979; Sakata and Katayama, 1987; 1988). Adsorption of counter-ion from bulk solution has been found to be important near a point on the adsorption isotherm when the intrinsic surface charge is neutralized (Bijsterbosch, 1974; Greenland and Quirk, 1962; Sexsmith and White, 1959).

A Donnan distribution (Sakata and Katayama, 1987; Westall, 1982a) or a cation-exchange model (Brown and Combs, 1985) can provide a useful representation of the effect of electrolyte type and concentration on organic cation adsorption. The ion-exchange model, which we have modified to include

adsorption of pyridinium chloride, treats the adsorption reactions as being electrically neutral within the adsorbing phase, and adequately describes the effect of added NaCl and $CaCl_2$ on adsorption of DP. The model is a special case of a Donnan equilibrium. A generalized Donnan distribution model can account for a pH-dependent charge in the Donnan phase. Our results suggest that natural sorbent materials behave more like the special case of ion-exchange than the general case with pH-dependent charge.

Distribution of organic cations in the environment. The results of this study and that of Brown and Combs (1985) suggest that it may be possible to estimate the environmental distributions of organic cations within reasonable limits, given the CEC of the sorbing phase, the effective chain length of the organic cation, and the concentrations of organic cation and other major ions in the system (both dissolved and adsorbed). Present uncertainties include: (i) the generality of the observed adsorption behavior of the three natural materials in this study; (ii) the variability of the distribution of adsorption site energies that can be expected for natural materials; (iii) the characterization of the adsorption of important metals that compete with organic cations; and (iv) the estimation of concentrations of co-ions that are adsorbed to particle surfaces. Complementary studies on the electrophoretic mobilities of natural particles under conditions of variable pH and adsorbed organic cation concentration could provide valuable information concerning the validity of the electrostatic model that we have proposed.

CONCLUSIONS

Large organic cations, such as dodecylpyridinium, are strongly adsorbed to sediment, soil, and subsurface materials. Adsorption depends primarily on the CEC of the sorbent material, the nature and concentration of the electrolyte, and the concentration and alkyl chain length of the organic cation. Solution pH has little effect on the adsorption of alkylpyridinium on the natural materials studied.

The adsorption isotherms are distinctly nonlinear, even at very low surface concentrations of organic cation. The data conform to the Freundlich equation. This behavior can be described by assuming a heterogeneous mixture of adsorption sites, and fitting the data with a summation of Langmuir isotherms. Evidence of hemimicelle formation was not seen in any of the isotherms conducted with natural materials.

Maximum or plateau adsorption values of adsorbed DP corresponded roughly to the reported CEC's of the sorbent materials. Adsorption was somewhat greater than the CEC for EPA-12 soil; this effect may be related to an increased role of organic matter for high f_{oc} materials.

Many features of the effect of electrolyte concentration on adsorption could be described by an ion-exchange model in which adsorption of ion pairs is also included. Ca^{2+} had a larger effect on adsorption than did Na^{+}; competitive adsorption with divalent metal cations will be important in affecting environmental distributions of large organic cations.

SECTION 4

INDIRECT EFFECTS OF ADSORPTION OF ALKYLPYRIDINIUM TO SOILS AND SUBSURFACE MATERIALS

INTRODUCTION

The adsorption of amphiphilic organic cations to soils and subsurface materials can have several indirect effects, the consequences of which depend on the particular environmental situation under consideration. Adsorption of organic cations can render mineral surfaces low in organic carbon much more attractive to hydrophobic organic compounds (Cowan and White, 1962; Mortland, 1975; Gaynor and Volk, 1976; Mortland et al., 1986; Bouchard et al., 1988), and can displace adsorbed metal ions (Beveridge and Pickering, 1983; Bouchard et al., 1988). While these processes will occur naturally as organic cations are introduced into the environment, they might also be the basis for remedial action at sites already contaminated with metals or hydrophobic organic compounds. Thus if amphiphilic organic cations were considered as a means of retarding the migration of hydrophobic pollutants through an aquifer, the counterpoint of enhancing the migration of metal ion already adsorbed to the aquifer material would also have to be considered. On the other hand, one might consider the use of amphiphilic organic cations to enhance the desorption of metal ions and to accelerate their removal in a pump-and-treat type operation; this approach is particularly appealing if a suitable degradable organic cation is used. Additionally, if the organic cations are introduced at super-micelle-concentrations, the possibility

exists to enhance *desorption* rather than *adsorption* of hydrophobic organic compounds as well. Thus a wide range of questions on the environmental chemistry of amphiphilic organic cations exist depending on whether the compounds are introduced as waste or as part of a treatment program, and whether the goal is to enhance or to retard the mobility of other pollutants, and whether the other pollutants behave more like metal ions or more like hydrophobic organic compounds.

This study addresses fundamental issues that are important in answering any of the questions above. Here we report on the results of experiments on distributions in (i) aqueous slurries with dodecylpyridinium, Lula aquifer material, and Cu(II) as a representative transition metal; and (ii) aqueous slurries with dodecylpyridinium, Lula aquifer material, and chlorobenzenes, as representatives of hydrophobic organic compounds. The results of this study illustrate the kinds of interactions that are to be expected and the magnitudes of their extents; for application to any particular environmental problem, additional site-specific investigations should be made. Of particular interest is the long-term adsorption-desorption kinetics of the organic cations under flow conditions.

METHODS

Adsorption of Cu(II). Two procedures were developed for investigating the effect of dodecylpyridinium on the adsorption of Cu(II) on Lula aquifer material:

1. Conventional batch adsorption experiments with Cu(II), DP, and Lula N6. Adsorption isotherms of Cu(II) on Lula N6 in 0.01 M NaCl at pH 5 were obtained with various concentrations of dodecylpyridinium. The concentration range of Cu(II) in solution was 1 - 100 μM, and the concentration of dodecylpyridinium was varied from no effect to strong displacement of Cu(II). Cu(II) and DP, in solution and on the sorbent, were determined by our standard procedures.

2. Discrete additions of DP to Cu(II) and Lula N6 in a pH-stat. The Lula N6 was placed in a pH-stat at pH 5 in 0.01 M $NaNO_3$ with a known amount of Cu(II); aliquots of dodecylpyridinium were added and the change in Cu(II) concentration was monitored with a cupric ion-selective electrode. This method was more versatile and allowed for more precise control of pH, but was technically more difficult to set up the first time. These experiments were carried out initially at pH 5 to reduce problems associated with formation of hydroxide complexes of Cu(II) and precipitation of $Cu(OH)_2(s)$. (The solubility product of $Cu(OH)_2(s)$ is $K_{sp} = (Cu^{2+})\ (OH^-)^2 = 10^{-19.4}$)

The advantage of the first procedure is that the concentration of DP in solution and on the surface is determined simultaneously with the concentration of Cu(II); the disadvantage of this procedure is that there is no control over pH during the time of batch equilibration. While the

adsorption of DP is relatively independent of pH, the adsorption of Cu(II) depends strongly on pH.

In the second procedure, the pH can be controlled extremely well (± 0.03 pH units), but the amount of Cu(II) on the sorbent must be determined by difference rather than by direct analysis, and the distribution of DP is found from a separate set of experiments.

Batch procedure for Cu(II) adsorption. The procedure for these experiments was similar to the standard procedure for DP adsorption described in the preceding section of this report. In each experiment, 100 mg of Lula N6 was added to 20 mL of 0.01 M NaCl in a centrifuge tube; then Cu(II) and DP were added to obtain adsorption isotherms of Cu(II) at several total concentrations of DP (0, 1, 10, 50, 100, 400, 1000 μM). The total amount of Cu(II) added was enough to give final Cu(II) concentrations in solution between 0 and 100 μM.

The tubes were shaken for 12 hours at 25° C and 500 RPM on a New Brunswick Model G-24 shaker, and then centrifuged for 1 hour at 11,000 RCF (10,000 RPM) and 25 °C on an IEC B-20 centrifuge.

Duplicates of each composition were run. The contents of one of the duplicates contained ^{14}C-labeled DP, and was used for determination of DP concentrations on the surface and in solution. The contents of the other duplicate, with unlabeled DP, was analyzed for Cu(II), both in solution and on the surface. Solution phase Cu(II) concentrations were determined directly by atomic adsorption spectrophotometry, and surface concentrations were determined after extraction into 0.01 M HNO_3. Recoveries of Cu were near 100% by this method. In addition, the pH of each solution was determined before and after equilibration. The goal was to have the solutions at pH 5 for comparison to the pH-stat study, but the actual pH values ranged from about 4.9 to 5.6.

pH-stat procedure for Cu(II) adsorption. A computer controlled two-electrode two-buret pH-stat was used to control pH and add Cu(II) to suspensions of DP and Lula N6 in 0.01 M $NaNO_3$. Cu(II) activity was monitored with an Orion Model 94-29-00 cupric ion-selective electrode (Cu(II)-ISE), and pH with an Ingold Model U-202-K7 glass electrode. An Orion Model 90-02-00 double junction reference electrode with 1 M KNO_3 in the outer sleeve and Orion Model 90-00-02 inner filling solution in the inner sleeve was used. Cell potentials were determined with Keithley Model 617 electrometers and transferred to a IBM-compatible PC over an IEEE-488 bus. The computer controlled the pH-stat function, the addition of aliquots of Cu(II) to the suspension, and monitored the approach of the Cu(II)-ISE to an operationally defined "equilibrium" condition (change in electrode potential less than, in general, 1 $\mu V\ s^{-1}$) after each addition of Cu(II). The cell was maintained at 25°C with a water jacket and blanketed with N_2. The electrolyte $NaNO_3$ was used instead of NaCl on account of the interference of Cl^- with the Cu(II)-ISE.

The pH-stat was maintained at pH 5 in all experiments. The pH-stat worked very well and maintained the pH within $\pm$ 0.03 units of the set value. The glass electrode was calibrated by addition of HNO_3 to the 0.01 M $NaNO_3$ electrolyte; thus the pH 5 refers strictly to concentration rather than activity. The Cu(II)-ISE was calibrated by addition of Cu(II) to the 0.01 M $NaNO_3$ electrolyte maintained at pH 5. The electrodes were calibrated immediately before and immediately after the exposure of the electrodes to Lula N6 and the DP; the exposure to the suspension appeared to have no significant effect on the response of the electrodes, and the before- and after- calibration data were pooled.

The suspensions contained 125 mg Lula N6 in 25 mL of 0.01 M $NaNO_3$ (5 g L^{-1}) plus either 0, 10, 50, 100, 400, or 1000 μM DP. To these suspensions was added Cu(II) to yield equilibrium concentrations in solution between 0 and about 100 μM Cu(II). The concentration of Cu(II) on the surface was determined by difference between total Cu(II) added and Cu(II) found in solution. The complexation of Cu(II) by OH^- is negligible at pH 5.

Adsorption of chlorobenzenes. The adsorption of chlorobenzenes to Lula N6 aquifer material, with varying surface concentrations of DP, was determined in conventional batch experiments. The chlorobenzenes were 1,2-dichlorobenzene, 1,2,3-trichlorobenzene, 1,2,3,4-tetrachlorobenzene, and pentachlorobenzene. The following procedure was used to prepare slurries that contained 25 g L^{-1} of Lula N6, total DP concentrations between 60 μM and 40 mM, and the chlorobenzenes at total concentrations approximately 1/100 of their solubility.

The experiments were carried out in centrifuge tubes with teflon-lined caps. To centrifuge tubes containing 0.500 g of washed Lula N6 were added 10 mL of 0.01 M NaCl solution with various concentrations of DP. These slurries were shaken for 4 hours at 500 RPM at 25°C, then 10 mL of 0.01 M NaCl containing the chlorobenzenes was added.

The slurries were again shaken for 4 hours at 500 RPM at 25°C and then centrifuged for 30 minutes at 10000 RCF (8900 rpm). The solution phase was then analyzed for chlorobenzenes and DP.

The analysis of the chlorobenzenes was by gas chromatography with electron capture detection. The chlorobenzenes were extracted from 2 mL of the aqueous phase (to which 0.05 g NaCl had been added) into 1 mL of hexane to which an internal standard had been added. The amount of the

chlorobenzenes on the sorbent was determined by difference. The solution concentration of DP was determined by UV spectrophotometry and the amount of DP on the sorbent was determined by difference. Generally we try to determine both solution and sorbed concentrations directly, but in these experiments thoroughness yielded to expediency. However, in selected experiments we did find that recoveries were generally very good and that determination of surface concentrations by difference is generally a valid approach for these systems. Blanks with and without DP showed 0 - 5 % loss of chlorobenzenes to the walls or to the head space.

RESULTS AND DISCUSSION

Adsorption of Cu(II) on Lula N6. The adsorption isotherm of Cu(II) on Lula N6 in 0.01 M NaCl, in the absence of DP, is quite nonlinear, as shown in Figure 8. (The isotherms in the figure are from the batch experiments; the isotherms from the pH-stat experiments were quite similar and are not shown.) The apparent distribution ratio (D_c) varies between 2000 and 100 L kg^{-1} for solution concentrations between 5 and 100 μM. Over this range of solution concentrations the surface concentrations range between 1 and 10 mmol kg^{-1}, which is still far below an apparent cation exchange capacity of the sorbent. Solution concentrations were held below 200 μM and pH below 5.5 in these experiments to avoid problems with precipitation of $Cu(OH)_2$.

The effect of DP on Cu(II) adsorption. Adsorption isotherms of Cu(II) with various total concentrations of DP are shown in Figure 8, both on a logarithmic and a linear scale. (The *total concentration* refers to the total number of moles of DP added per liter of solution; this is not the same as the final equilibrium concentration in solution. The approximate relation between total and adsorbed DP is given in Table 4.) The effect of DP is to depress the adsorption of Cu(II) significantly. The data shown in Figure 8 are from the batch experiments, in which concentrations of DP and Cu(II), both in solution and on the surface, were determined directly; the pH generally ranged between 5.5, at low Cu(II) concentrations, and 5.0, at high Cu(II) concentrations.

Before the effect of DP on the adsorption of Cu(II) can be addressed, the effect of Cu(II) on the adsorption of DP must be understood, i.e., how do the surface and solution concentrations of DP vary with addition of Cu(II), at constant total concentration of DP?

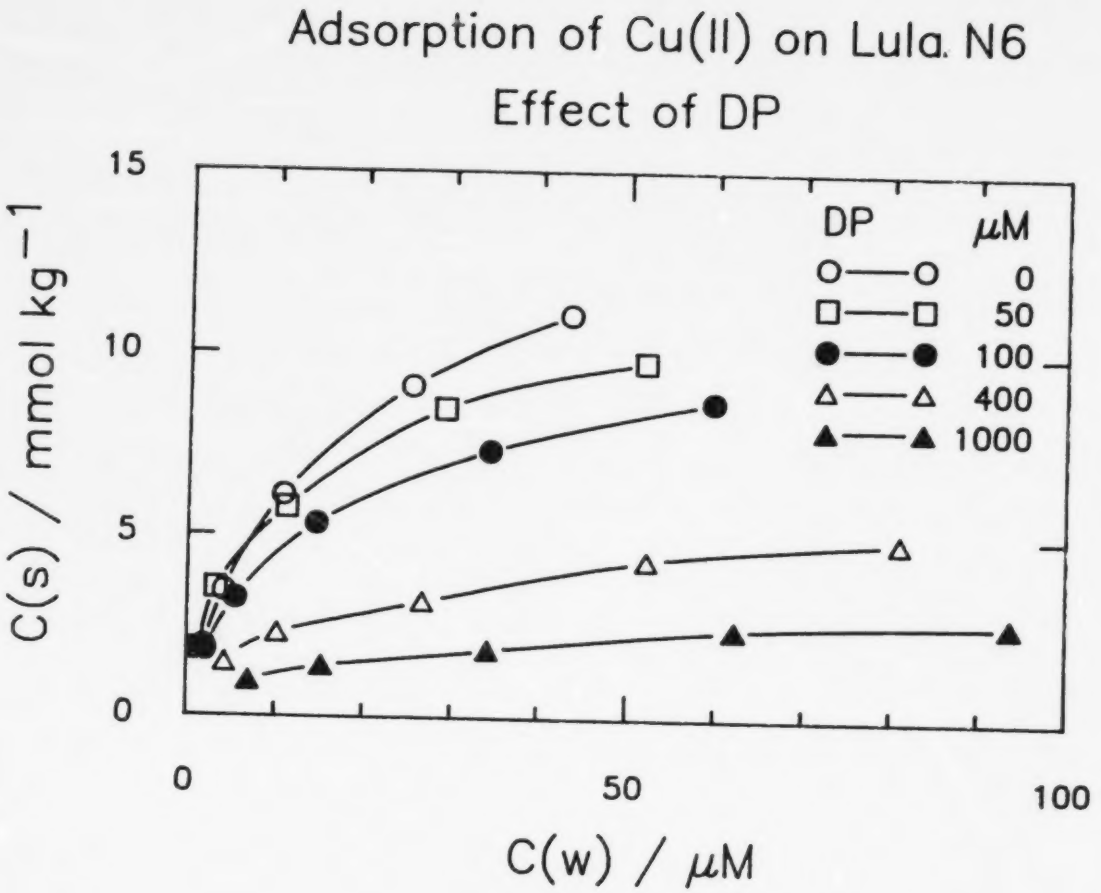

Figure 8. Adsorption of Cu(II) on Lula N6 (0.005 kg L^{-1}) in 0.01 NaCl at pH in the range about 4.9 - 5.6, with various total concentrations of DP (given on the figure), shown on linear and logarithmic scales. The approximate relation between total and adsorbed DP is given in Table 4. Total Cu(II) was in the range 10 - 200 μM for the isotherms. Isotherms were obtained from the batch method, in which both solution and adsorbed Cu(II) and DP were determined directly.

Figure 8A. Isotherm on linear scale.

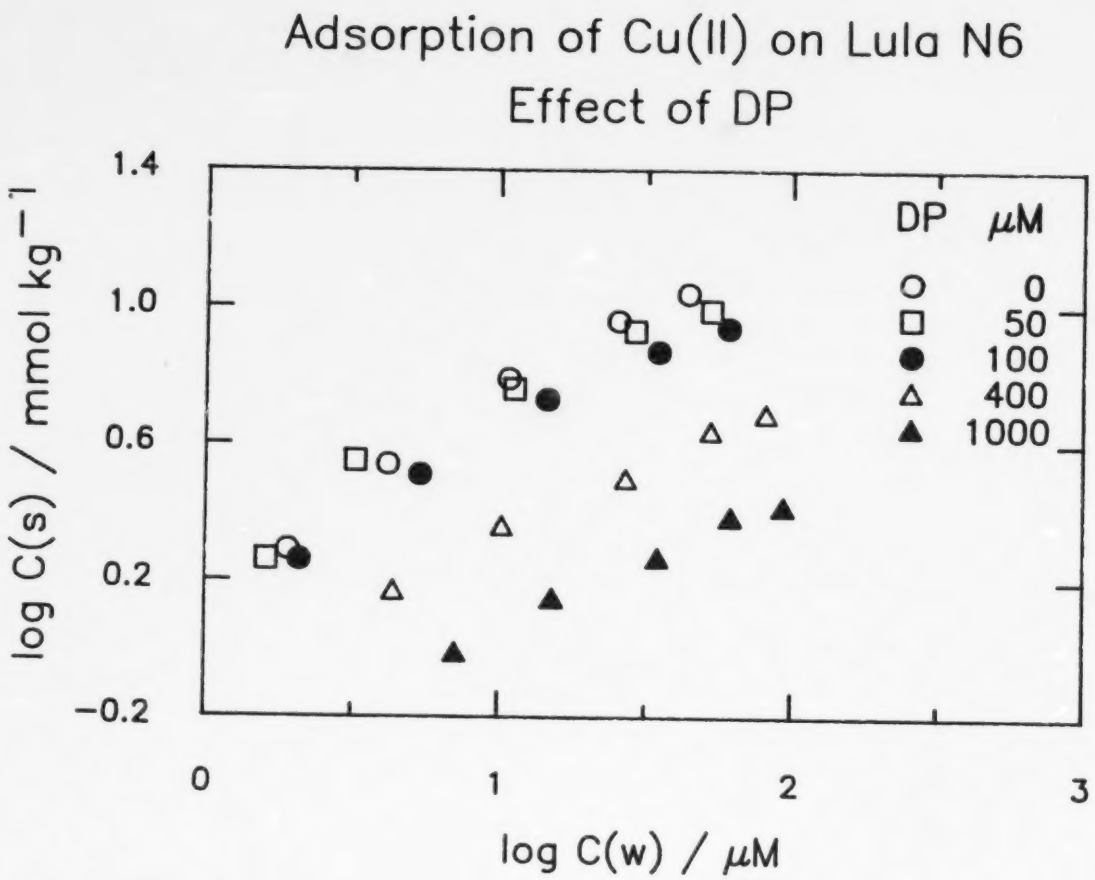

Figure 8B. Isotherm on logarithmic scale.

Table 4. Range of Concentration of DP in solution and on the surface over the course of Cu(II) adsorption isotherms.

Total concentration in solution (initial) μM	Solution concentration at equilibrium μM	Surface concentration at equilibrium mmol kg^{-1}
1	0.016 - 0.020	0.180 - 0.183
10	0.355 - 0.424	1.83 - 1.87
50	3.19 - 4.26	8.46 - 9.03
100	12.2 - 15.0	17.0 - 17.5
400	206 - 229	34.0 - 36.6
1000	778 - 805	39.9 - 42.4

Cu(II) has very little effect on the adsorption of DP over the range of conditions that were studied, as shown in Table 4. Over the course of any isotherm, the surface concentration of DP varied generally less than about 5%. At low total concentrations of DP ($T_{DP} \leq 50$ μM), almost all of the DP was adsorbed, but the concentrations of DP and Cu(II) on the surface were still apparently so low that there was little interaction. At higher concentrations of DP ($T_{DP} \geq 400$ μM), surface concentrations of DP and Cu(II) were of the same order of magnitude and close to the apparent CEC of the sorbent; however, the presence of Cu(II) still had a small effect on the distribution of DP.

In contrast, the DP had a strong effect on the adsorption of Cu(II), particularly above 100 μM total DP (or 17 mmol kg^{-1} DP on the sorbent). At 400 and 1000 μM total DP, the DP concentrations on the surface were close to the apparent CEC determined by DP adsorption; only under these conditions did the moles of DP desorbed per mol of Cu(II) adsorbed approach the stoichiometric 2:1 limit characteristic of an electroneutral ion exchange.

Discussion. The interactions in the system Cu(II), DP, Lula N6 are complicated: the isotherms are nonlinear, Cu(II) adsorption depends on pH, and there is little evidence for electroneutral ion exchange. The reactions that are likely to explain the behavior in this system are ion exchange of DP for Na^+ over most of the range, the adsorption of DP with Cl^- as a counter-ion as a secondary process, adsorption of Cu(II) by a pH dependent surface complexation reaction, with a weak electrostatic coupling to the DP adsorption. Further investigation of this system is required to shed light on the mechanism of adsorption of Cu(II) and other metal ions as well, in particular on the importance of the electrostatic energy in the adsorption of metals to natural sorbents.

This work is relevant to two environmental questions: (i) the use of amphiphilic organic cations to enhance the ability of inorganic substrates to retain hydrophobic organic compounds, and the concomitant undesirable side effect of enhancing metal ion mobility, and (ii) the use of amphiphilic organic cations to enhance desorption of metal ions in pump-and-treat type operations.

It is clear that the amphiphilic organic cations could be used to promote desorption of metal cations. For example, with 1000 μM total DP in the system, the D_c of Cu(II) is about one tenth of its value with no DP, with the same total amount of Cu(II) in the system; at 400μM total DP, the drop in D_c of Cu(II) is to about one fourth. Indications are that this drop depends on the surface concentration of DP relative to the CEC of the sorbent. Since Cu(II) does seem to cause some desorption of DP at concentrations near the CEC, it is possible that another organic cation that adsorbs more strongly (such as tetradecyl- or hexadecylpyridinium) could displace Cu(II) more effectively.

Another factor to consider in the selection of organic cations is the adsorption-desorption kinetics under conditions of flow through a porous medium; further work on this subject is under way.

Effect of DP on the adsorption of chlorobenzenes by Lula N6. The concentration distribution ratio (D_c) of the chlorobenzenes, as a function of the concentration of DP on the surface, is shown in Figure 9. Clearly the presence of DP on the surface enhances the adsorption. (However, at sufficiently high concentrations of DP, micelles are formed in solution and the D_c falls off again. These data are not shown in the figure.)

It is significant that the value of D_c climbs not linearly with concentration of DP on the surface (and fractional organic-carbon content of

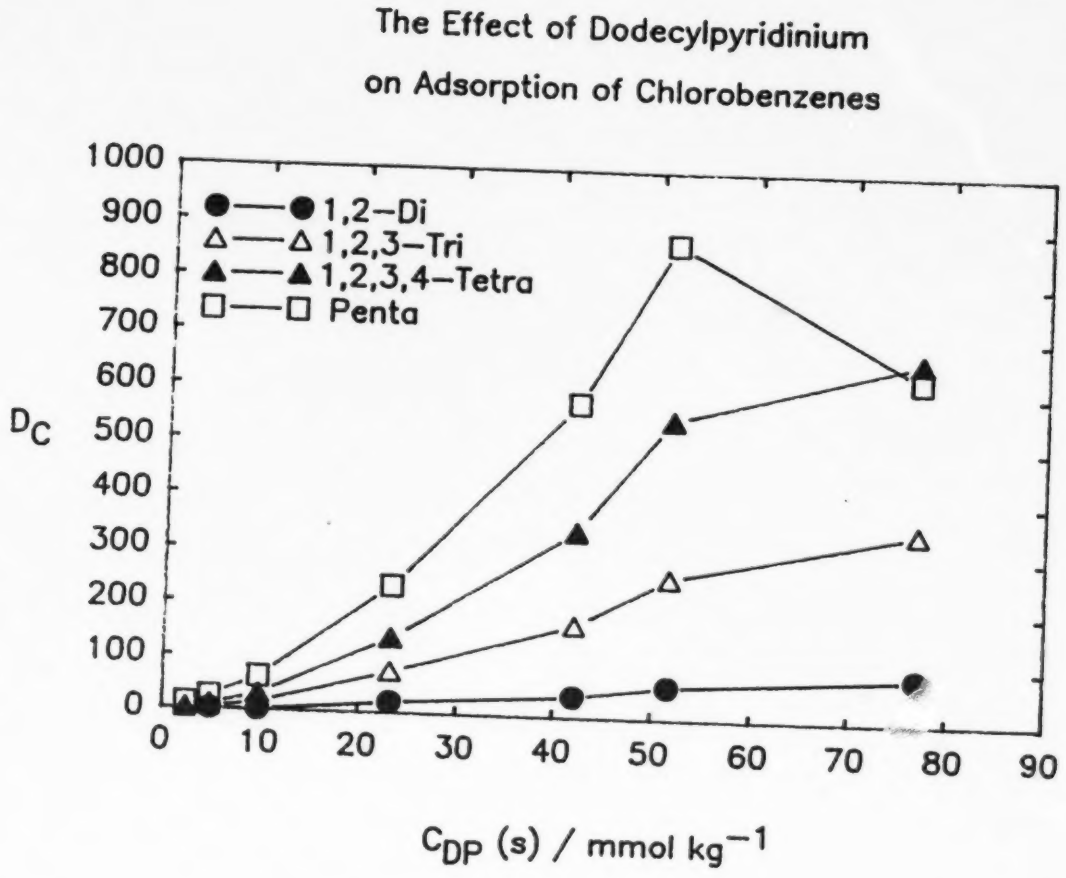

Figure 9. Concentration distribution ratios (D_c) of chlorobenzenes between Lula N6 (0.025 kg L^{-1}) and 0.01 M NaCl, as a function of amount of DP on the sorbent.

the sorbent, f_{oc}) but almost quadratically, particularly for the chlorobenzenes with greater numbers of Cl^- substituents. Thus the "quality" of organic carbon for adsorbing hydrophobic compounds increases with surface coverage. One could associate this behavior with the formation of hydrophobic domains on the surface; the higher the surface coverage the greater the likelihood that aggregates of DP are situated to interact with a chlorobenzene molecule.

The range of experimentally determined values of D_c can be compared to those predicted from the K_{ow}-f_{oc} paradigm,

$$\log D_c = a \log K_{ow} + \log f_{oc} + b \qquad (11)$$

For this comparison we use the values of a, b, and K_{ow} values from the correlation of Schwarzenbach and Westall (1981), which was derived with chlorobenzenes and alkylbenzenes. The f_{oc} of the sorbent is found from the mass of carbon in a mole of DP (204 g / mol) and the concentration of DP on the surface (mol / kg). The values of D_c predicted from Equation 11 are all lower than those found experimentally for the DP-treated Lula N6.

It is clear that organic cations could be used to increase the organic carbon content and the ability of an inorganic substrate to retain a hydrophobic compound, with as little as 10 mmol kg^{-1} (0.2% organic carbon for the sorbent). At this level the distribution of Cu(II) is affected, but not severely. Thus by fine tuning the hydrophobicity of the organic cation to the specific environmental problem (properties of the sorbent, properties of the hydrophobic solutes, etc.), it may be possible to enhance retention of hydrophobic compounds without significantly enhancing mobility of toxic cations.

CONCLUSIONS

The adsorption of DP to Lula aquifer material enhances the desorption of Cu(II). The enhanced desorption occurs when the surface concentration of DP is within 10 - 100% of the adsorption maximum of DP (an effective CEC) in the electrolyte which was used, 0.01 M NaCl. However, the reaction cannot be described as a simple ion exchange reaction; pH-dependent surface complexation of Cu(II) and electrostatic competition with DP seems to be involved.

The adsorption of DP to Lula aquifer material enhances sorption of chlorobenzenes. DP loadings equivalent to f_{oc} = 0.0001 - 0.005 were examined. Over this range, the values of K_{oc} were not constant, but were greater for greater loadings of DP. This result is attributed to cooperative effects of DP molecules at higher surface concentrations.

The possibility of using amphiphilic organic cations in the subsurface environment to alter the mobility of pollutant metal ions or pollutant hydrophobic organic compounds appears to be worthy of further study. However, further laboratory study and site-specific information is still necessary for the development of a treatment program.

SECTION 5

CONCLUSIONS AND RECOMMENDATIONS

Large organic cations, such as dodecylpyridinium, are strongly adsorbed to sediment, soil, and subsurface materials. Adsorption depends primarily on the CEC of the sorbent material, the nature and concentration of the electrolyte, and the concentration and alkyl chain length of the organic cation. Solution pH has little effect on the adsorption of alkylpyridinium on the natural materials studied.

The adsorption isotherms are distinctly nonlinear, even at very low surface concentrations of organic cation. The data conform to the Freundlich equation and can be interpreted mechanistically as a summation of Langmuir isotherms.

Maximum or plateau adsorption values of adsorbed DP corresponded roughly to the reported CEC's of the sorbent materials. Adsorption was somewhat greater than the CEC for EPA-12 soil; this effect may be related to an increased role of organic matter for high f_{oc} materials.

The effects of electrolyte concentration on adsorption could be explained with two types of electroneutral reactions: cation exchange and adsorption of the organic cation with an inorganic anion. Ca^{2+} had a larger effect on adsorption than did Na^{+}, as expected for ion exchange.

The adsorption of DP to Lula aquifer material displaces Cu(II). The displacement occurs when the surface concentration of DP is within 10 - 100% of the adsorption maximum of DP (an effective CEC) in 0.01 M NaCl. However,

the reaction cannot be described as a simple ion exchange reaction; pH-dependent surface complexation of Cu(II) and electrostatic competition with DP seem to be involved.

The adsorption of DP to Lula aquifer material promotes sorption of chlorobenzenes. Over the range of DP equivalent to f_{oc} = 0.0001 - 0.005, the values of K_{oc} were not constant, but were greater for greater loadings of DP. This result is attributed to cooperative effects of DP molecules at higher surface concentrations.

This work is relevant to two potential site-remediation methodologies: (i) the use of amphiphilic organic cations to increase the tendency of inorganic substrates to retain hydrophobic organic compounds, and (ii) the use of amphiphilic organic cations to promote desorption of metal ions in pump-and-treat type operations. However, further study and site-specific information is still necessary for the development of a treatment program.

Recommendations. For further study we recommend that efforts be concentrated on: (i) the nature of competition in the system organic cation / NaCl, $CaCl_2$ / transition metal cation, i.e., clarification of the role of electrostatic and surface-complexation interactions in the sorption of organic cations and metal cations on heterogeneous sorbents; (ii) the role of the "quality" of organic carbon in the sorption of hydrophobic solutes such as chlorobenzenes, and the dependence of apparent D_c on coverage of the surface by organic cations; (iii) adsorption-desorption kinetics of organic cations in soil-column experiments, and the concomitant effect on metal ion and hydrophobic organic compound adsorption-desorption; and (iv) the effect of organic cations on the hydraulic conductivity of soil columns.

SECTION 6

LITERATURE CITED

Adamson, A. W. 1976. Physical Chemistry of Surfaces, 3rd Ed. New York: Wiley. p. 389.

Baleux, B. and P. Caumette. 1977. Biodegradation de Quelques Agents de Surface Cationiques. Water Res. 11:833-841.

Bayer, O., H. Hoffman and W. Ulbricht. 1986. The Influence of Solubilized Additives on Surfactant Solutions Containing Rodlike Micelles. In Surfactants and Solutions, Volume 4, ed. K. L. Mittal and P. Bothorel, pp. 343-348. New York: Plenum.

Beveridge, A. and W. F. Pickering. 1983. The Influence of Surfactants on the Adsorption of Heavy Metal Ions by Clays. Water Res. 17:215-225.

Bijsterbosch, B. H. 1974. Characterization of Silica Surfaces by Adsorption from Solution. Investigations into the Mechanism of Adsorption of Cationic Surfactants. J. Colloid Interface Sci. 47:186-198.

Boethling, R. S. 1984. Environmental Fate and Toxicity in Wastewater Treatment of Quaternary Ammonium Surfactants. Water Res. 18:1061-1076.

Bouchard, D. C., R. M. Powell and D. A. Clark. 1988. Organic Cation Effects on the Sorption of Metals and Neutral Organiuc Compounds on Aquifer Material. J. Environ. Sci. Health. A23:585-601.

Brown, D. S. and G. Combs. 1985. A Modified Langmuir Equation for Predicting Sorption of Methylacridinium Ion in Soils and Sediments. J. Environ. Qual. 14:195-199.

Brownawell, B. J., J. Collier, C. Hua and J. C. Westall. In prep. for Environ. Sci. Technol.

Connor, P. and R. H. Ottewill. 1971. The Adsorption of Cationic Surface Active Agents on Polystyrene Surfaces. J. Colloid Interface Sci. 37:642-651.

Cowan, C. T. and D. White. 1962. Adsorption by Organo-Clay complexes. In Proceedings of the Ninth National Conference on Clays and Clay Minerals, 1960, ed. A. Swineford, pp. 459-467. New York: Pergamon.

Davis, J. A. and R. Gloor. 1981. Adsorption of Dissolved Organics in Lake Water by Aluminum Oxide. Effect of Molecular Weight. Environ. Sci. Technol. 15:1223-1229.

DellaGuardia, R. A. and J. K. Thomas. 1983. Photoprocesses on Colloidal Clay Systems. 2. Quenching Studies and the Effect of Surfactants on the Luminescent Properties of Pyrene Derivatives Adsorbed on Clay Colloids. J. Phys. Chem. 87:3550-3557.

Ford, W. P. J., R. H. Ottewill and H. C. Parreira. 1966. Light-Scattering Studies on Dodecylpyridinium Halides. J. Colloid Interface Sci. 21:522-533.

Fuerstenau, D. W. 1956. Streaming Potential Studies on Quartz Solutions of Aminium Acetates in Relation to the Formation of Hemi-Micelles at the Quartz-Solution Interface. J. Phys. Chem. 60:981-985.

Fuerstenau, D. W. and H. J. Modi. 1959. Streaming Potentials of Corundum in Aqueous Organic Electrolyte Solutions. J. Electochem. Soc. 106:336-341.

Fuerstenau, D. W., T. W. Healy and P. Somasundaran. 1964. The Role of the Hydrocarbon Chain of Alkyl Collectors in Flotation. Trans. AIME. 229:321-325.

Fuller, C. C. and J. A. Davis. 1987. Processes and Kinetics of Cd^{2+} Sorption by a Calcareous Aquifer Sand. Geochim. Cosmochim. Acta. 51:1491-1502.

Games, L. M., J. E. King and R. L. Larson. 1982. Fate and Distribution of a Quaternary Ammonium Surfactant, Octadecyltrimethylammonium Chloride (OTAC), in Wastewater Treatment. Environ. Sci. Technol. 16:483-488.

Gaynor, J. D. and V. V. Volk. 1976. Surfactant Effects on Picloram Adsorption by Soils. Weed Sci. 24:549-552.

Ghosal, D. N. and S. K. Mukherjee. 1972. Studies on the Sorption of Crystal Violet on and from Bentonite and Kaolinite. J. Indian Chem. Soc. 49:569-572.

Greenland, D. J. and J. P. Quirk. 1962. Adsorption of 1-n-Alkylpyridinium Bromides by Montmorillonite. In Proceedings of the Ninth National Conference on Clays and Clay Minerals, 1960, ed. A. Swineford, pp. 484-499. New York: Pergamon Press.

Greek, B. F. and P. L. Layman. 1989. Higher Costs Spur New Detergent Formulations. Chem. Eng. News. 67(4):29-49.

Gschwend, P. M.and S. C. Wu. 1985. On the Constancy of Sediment-Water Partition Coefficients of Hydrophobic Organic Pollutants. Environ. Sci. Technol. 16:594-602.

Hand, V. C. and G. K. Williams. 1987. Structure-Activity Relationships for Sorption of Linear Alkylbenzenesulfonates. Environ. Sci. Technol. 21:370-373.

Harrop, R. 1978. The Adsorption of Cetyl Pyridinium Bromide on Silica. Surface Technol. 7:81-90.

Hassett, J. J., J. C. Means, W. L. Banwart and S. G. Wood. 1980. Sorption Properties of Sediments and Energy-Related Pollutants. Report No. EPA-600/3-80-041. Springfield, VA: National Technical Information Service, U.S. Environmental Protection Agency.

Hayes, M. B., M. E. Pick and B. A. Toms. 1978. The Influence of Organocation Structure on the Adsorption of Mono- and Bipyridinium Cations by Expanding Lattice Clay Minerals. I. Adsorption by Na^+-Montmorillonite. J. Coll. Interface Sci. 65:254-265.

Horrocks, D. L. 1977. The H Number Concept. Technical Report No. 1095-NUC-77-1T. Fullerton, CA: Beckman Instruments Inc.

Hough, D. B. and H. M. Rendall. 1983. Adsorption of Ionic Surfactants. In Adsorption from Solution at the Solid/Liquid Interface, ed. G. D. Parfitt and C. H. Rochester. pp 247-319. London: Academic Press.

Huang, Z. and T. Gu. 1987. Mixed Adsorption of Nonionic and Cationic Surfactants on Silica Gel and Methylated Silica Gel. Colloids Surfaces. 28:159-168.

Huber, L. H. 1984. Ecological Behavior of Cationic Surfactants from Fabric Softeners in the Aquatic Environment. J. Amer. Oil Chem. Soc. 61:377-382.

Iler, R. K. 1979. The Chemistry of Silica. New York: Wiley.

Karickhoff, S. W. and D. S. Brown. 1978. Paraquat Sorption as a Function of Particle Size in Natural Sediments. J. Environ. Qual. 7:246-252.

Karickhoff, S. W., D. S. Brown and T. A. Scott. 1979. Sorption of Hydrophobic Pollutants on Natural Sediments. Water Res. 13: 241-248.

Law, J. P., M. E. Bloodworth and J. R. Runkles. 1966a. Reactions of Surfactants with Montmorillonitic Soils. Soil Sci. Soc. Amer. Proc. 30:327-332.

Law, J. P. and G. W. Kunze. 1966b. Reaction of Surfactants with Montmorillonite: Adsorption Mechanisms. Soil Sci. Soc. Amer. Proc. 30:321-327.

Lee, J-F., J. R. Crum, S. A. Boyd. 1989. Enhanced Retention of Organic Contaminants by Soils Exchanged with Organic Cations. Environ. Sci. Technol. 23:1365-1372.

Lewis, M. A. and D. Suprenant. 1983. Comparative Acute Toxicities of Surfactants to Aquatic Invertebrates. Ecotoxicol. Environ. Safety. 7:313-322.

Lewis, M. A. and V. T. Wee. 1983. Aquatic Safety Assessment for Cationic Surfactants. Environ. Toxicol. Chem. 2:105-118.

Malik, W. U., S. K. Srivastava and D. Gupta. 1972. Studies on the Interaction of Cationic Surfactants with Clay Minerals. Clay Minerals. 9:369-382.

Mortland, M. M. 1975. Interaction between Clays and Inorganic and Organic Pollutants. In Proceedings of the International Clay Conference, Mexico City, Mexico, July 16-23, ed. S. W. Bailey, pp. 469-475. Wilmette, Ill.: Applied Pub. LTD.

Mortland, M. M., S. Shaobai and S. A. Boyd. 1986. Clay-Organic Complexes as Adsorbents for Phenol and Chlorophenols. Clays and Clay Minerals, 34:581-585.

Nakamura, T. and J. K. Thomas. 1986. The Interaction of Alkylammonium Salts with Synthetic Clays. A Fluorescence and Laser Excitation Study. J. Phys. Chem. 90:641-644.

Narine, D. R. and R. D. Guy. 1981. Interactions of Some Large Organic Cations with Bentonite in Dilute Aqueous Systems. Clays and Clay Minerals. 29:205-212.

Ottewill, R. H. and M. C. Rastogi. 1960. The Stability of Hydrophobic Sols in the Presence of Surface-Active Agents. Part 3. -An Examination by Microelectrophoresis of the Behaviour of Silver Iodide Sols in the Presence of Cationic Surface-Active Agents. Trans. Faraday Soc. 56:880-892.

Philen, O. D., Jr., S. B. Weed and J. B. Weber. 1970. Estimation of Surface Charge Density of Mica and Vermiculite by Competitive Adsorption of $Diquat^{2+}$ vs. $Paraquat^{2+}$. Soil Sci. Soc. Amer. Proc. 34:527-531.

Philen, O. D., Jr., S. B. Weed, and J. B. Weber. 1971. Surface Charge Characterization of Layer Silicates by Competitive Adsorption of Two Organic Divalent Cations. Clays and Clay Minerals. 19:295-302.

Qawas, A., I. Y. M. Fulayyeh, J. Lyall, J. B. Murray, and G. Smith. 1986. The Adsorption of Bactericides by Solids and the Fitting of Adsorption Data to Langmuir Equation by a Nonlinear Least-Squares Method. Pharm. Acta Helv. 61:314-319.

Ralston, J. and J. A. Kitchener. 1975. The Surface Chemistry of Amosite Asbestos, and Amphibole Silicate. J. Colloid. Interface Sci. 50:242-249.

Rastogi, M. C. and B. L. Dhawan. 1974. Stabilization of Sandy Soils by Chemical Additives: Part I - Adsorption of Surface Active Agents at Soil/Water Interface. Indian J. Chem. 12:158-160.

Rendall, H. M., A. L. Smith and L. A. Williams. 1979. Electrokinetic Study of Surfactant Adsorption. J. Chem. Soc., Faraday Trans. 75:669-678.

Rupprecht, V. H., E. Ullmann, and K. Thoma. 1971. Auswirkungen von Elekrolyten auf das Sorptionsvermogen kolloider Kieselsaure Aerosil. Fortschr. Kolloide u. Polymere. 55:45-48.

Sakata, K. and A. Katayama. 1987. The Absorption of Ionic Surfactants in Vinylon and Acetate. J. Colloid Interface Sci. 116:177-181.

Sakata, K. and A. Katayama. 1988. The Influence of Different Electrolytes on the Absorption of Ionic Surfactants in Acetate Fibers. J. Colloid Interface Sci. 123:129-135.

Saleeb, F. Z. and J. A. Kitchener. 1965. The Effect of Graphitization on the Adsorption of Surfactants by Carbon Black. J. Chem. Soc. 87:911-917.

Schwarz, R., K. Heckmann and J. Strnad. 1988. Adsorption Model of Pyridinium Salts on Quartz. J. Colloid Interface Sci. 124:50-56.

Schwarzenbach, R. P. and J. Westall. 1981. Transport of Nonpolar Organic Compounds from Surface Water to Ground Water. Environ. Sci. Technol. 15:1360-1367.

Sexsmith, F. H. and H. J. White, Jr. 1959. The Absorption of Cationic Surfactants by Cellulosic Materials. J. Colloid Interface Sci. 14:598-618.

Shimp, R. J. 1989. Adaptation to a Quaternary Ammonium Surfacant in Aquatic Sediment Microcosms. Environ. Toxicol. Chem. 8:201-208.

Somasundaran, P., T. W. Healy and D. W. Fuerstenau. 1964. Surfactant Adsorption at the Solid-Liquid Interface-Dependence of Mechanism on Chain Length. J. Phys. Chem. 68:3562-3566.

Takeda, S. and S. Usui. 1987. Adsorption of Dodecylammonium Ion on Quartz in Relation to its Flotation. Colloids Surfaces 23:15-28.

Tamamushi, B., and K. Tamaki. 1959. Trans. Faraday Soc. 55:1007-102?.

Tanford, C. 1980. The Hydrophobic Effect: Formation of Micelles and Biological Membranes. New York: Wiley-Interscience. pp 1-4.

Ter-Minassian-Saraga, L. 1966. Mecanisme de L'Adsorption d'un Cation, Alkyltrimethylammonium a L'Interface Silice-Eau. J. Chim. Phys. 63:1278-1280.

Theng, B. K. G., D. J. Greenland, and J. P. Quirk. 1967. Adsorption of Alkylammonium Cations by Montmorillonite. Clay Minerals. 7:1-17.

Theng, B. K. G., D. J. Greenland, and J. P. Quirk. 1968. The Effect of Exchangeable Alkylammonium Ions on the Swelling of Montmorillonite in Water. Clay Minerals. 7:271-293.

Travis, C. C. and E. L. Etnier. 1981. A Survey of Sorption Relationships for Reactive Solutes in Soil. J. Environ. Qual. 10:8-17.

van Olphen, H. and J. J. Fripiat, Eds. 1979. Data Handbook for Clay Materials and Other Non-Metallic Minerals. New York: Permagon.

Vilcu, R. and M. Olteanu. 1975. Adsorption of some Alkylpyridinium Chlorides at the Silica-Alumina-Water Interface. Revue Roumaine de Chimie. 20:1041-1050.

Weber, J. B., P. W. Perry, and R. P. Upchurch. 1965. The Influence of Temperature and Time on the Adsorption of Paraquat, Diquat, 2,4-D and Proetone by Clays, Charcoal, and an Anion-Exchange Resin. Soil Sci. Soc. Proc. 29:678-688.

Weber, J. B., T. M. Ward, and S. B. Weed. 1968. Adsorption and Desorption of Diquat, Paraquat, Prometone, and 2,4-D by Charcoal and Exchange Resins. Soil Sci. Soc. Amer. Proc. 32:197-200.

Weber, J. B., and S. B. Weed. 1968. Adsorption of Diquat, Paraquat, and Prometone by Montmorillonite and Kaolinite Clay Minerals. Soil Sci. Soc. Amer. Proc. 32:485-487.

Weed, S. B. and J. B. Weber. 1969. The Effect of Cation Exchange Capacity on the Retention of $Diquat^{2+}$ and $Paraquat^{2+}$ by Three-Layer Type Clay Minerals. I. Adsorption and Release. Soil Sci. Soc. Amer. Proc. 33:379-383, 1969.

Westall, J. C. 1982a. FITEQL: A Computer Program for Determinination of Chemical Equilibrium Constants from Equilibrium Data, Version 1.2. Report 82-01. Corvallis, OR: Oregon State University.

Westall, J. C. 1982b. FITEQL A Computer Program for Determinination of Chemical Equilibrium Constants from Equilibrium Data, Version 2.0. Report 82-02. Corvallis, OR: Oregon State University.

Westall, J. 1986. Reactions at the Oxide-Solution Interface: Chemical and Electrostatic Models. In Geochemical Processes at Mineral Surfaces, ed. J. A. Davis and K. F. Hayes, pp. 54-78. Symposium Series No. 323. Washington, DC: American Chemical Society.

Westall, J. 1987. Adsorption Mechanisms in Aquatic Surface Chemistry. Aquatic Surface Chemistry, Ed. W. Stumm, pp. 3-32. New York: Wiley.

Zhang, W., C. Hua, B. J. Brownawell and J. C. Westall. 1989. In prep. for Environ. Sci. Technol.